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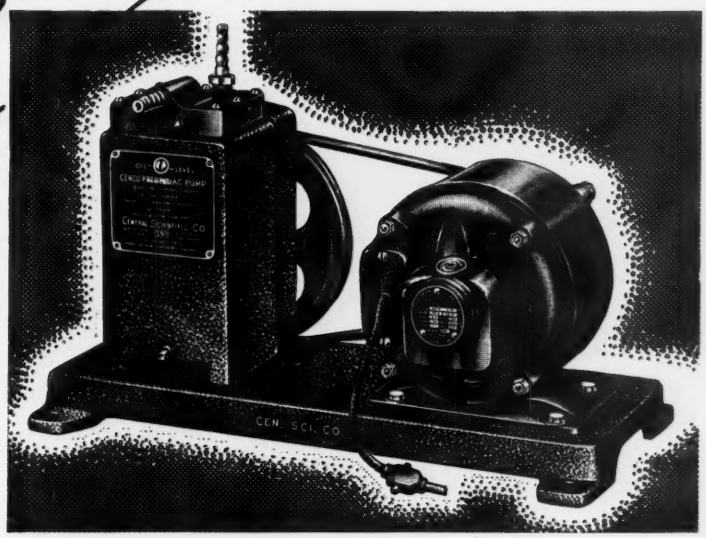

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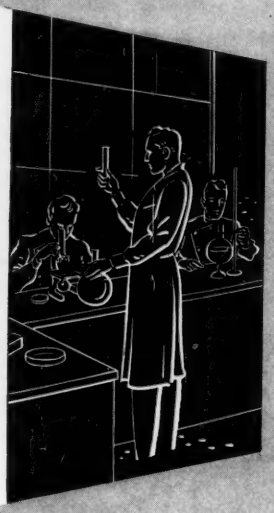

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Catalog News

Thermocouples

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If you haven't already received a copy, ask for Catalog N-33A(6). A copy will be sent by return mail.

Photometers

Photometric equipment users are finding much to interest them in L&N's newly revised catalog, "Photometers and Accessories."

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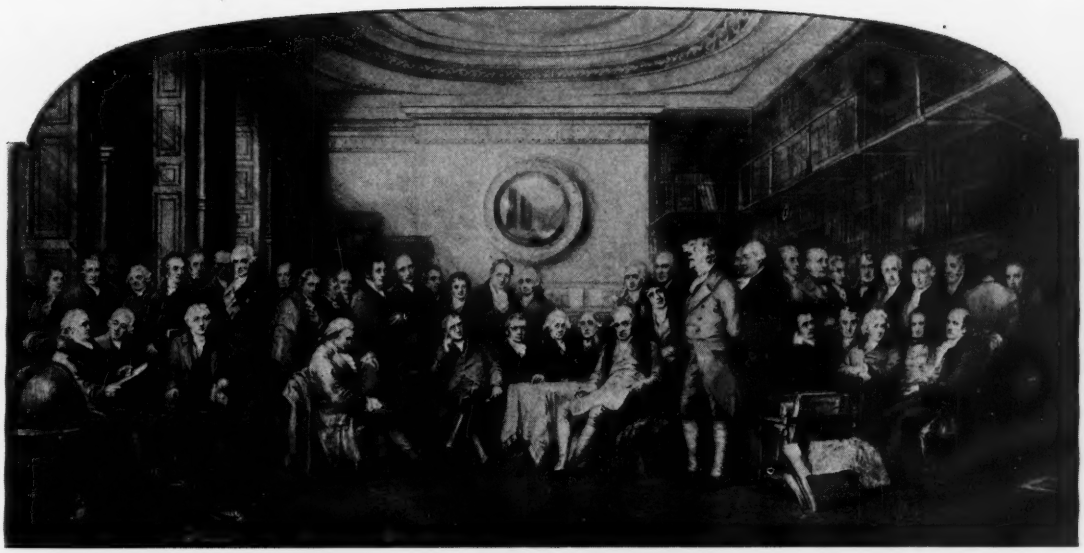

By permission of the National Portrait Gallery

Eminent Men of Science Living in 1807–8

Previous to the outbreak of the war this engraving, entitled "Eminent Men of Science Living in 1807–8," used to hang in salon XXVI of the National Portrait Gallery in London—rather inconspicuous in comparison with the well-known portraits of Davy, Faraday, Crookes, Darwin, Huxley, and many others.

The official catalog of 1914 of the Gallery has the following comment on the engraving:

"A group of 48 portraits, representing the most distinguished men in science, who were alive in 1807–8, assembled in the Library of the Royal Institution. This group was originated by William Walker, the engraver, who spent some years in collecting the most authentic likenesses possible of the persons represented. The grouping itself was designed by Sir John Gilbert, R.A., and the figures drawn by John Frederick Skill, the whole being finished by William Walker and his wife Elizabeth.

"This group was subsequently engraved by William Walker and G. Zobel, mezzotint-engraver. Certain alterations were made at the time of engraving, the figures of the Earl of Dundonald and Henry Fourdrinier being omitted, while those of William Chapman, 1749–1832, civil engineer, William James Frodsham, F.R.S., 1778–1850, chronometer maker, William Smith, LL.D., 1769–1839, geologist, Edward Troughton, F.R.A.S., 1753–1835, astronomical instrument maker, and Richard Watson, D.D., F.R.S., 1737–1836, Bishop of Llandaff, and professor of chemistry, were introduced."

The picture reproduced here is that of the engraving containing the portraits of the Earl of Dundonald and Henry Fourdrinier. Another copy of this engraving hangs in the hallway of the Royal Institution near the famous statue of Faraday.

(For an outline key to the figures in the picture, and accompanying brief biographical sketches, see "Eminent Men of Science Living in 1807–8," by H. Monmouth Smith, on page 203.)

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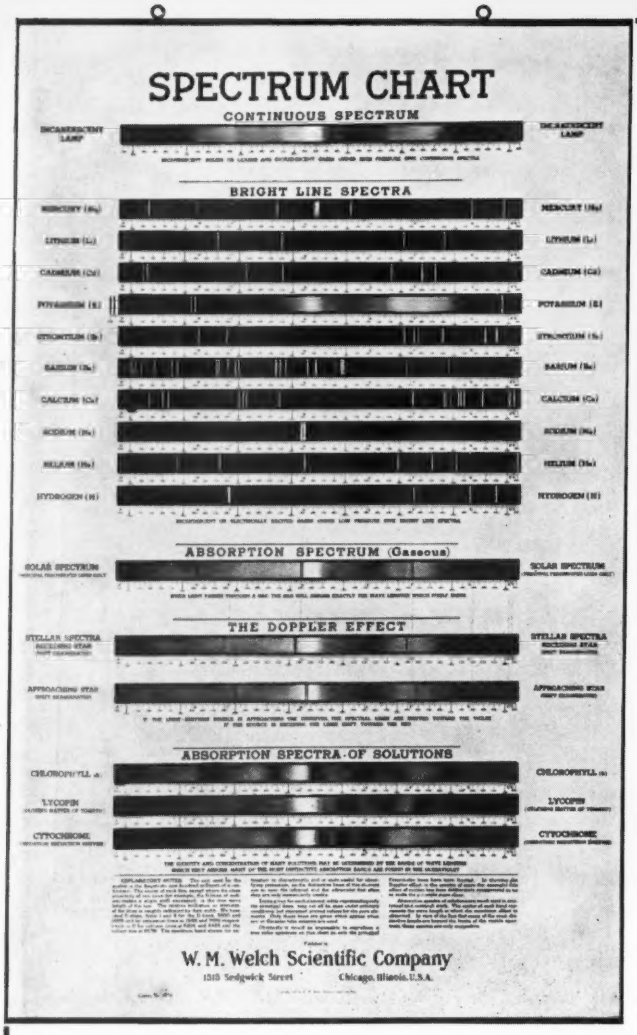

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Editor's Outlook

MUCH mental effort is being directed nowadays—and deservedly, we think—toward the solution of the problem of the General Course in chemistry. Only recently, we took part in the discussion in this very column. But there is a little angle which doesn't seem to have been turned. We can't think that it hasn't occurred to anyone; the alternative is that no one has wanted to face it seriously. So we will bring it out as though it were an idea of our own. It is a "Lady Godiva" sort of idea—you needn't look at it if you think you shouldn't: *Perhaps chemistry is getting to such a point that you can't teach it to everyone, after all.* We won't argue this point very enthusiastically, or we run the risk of arguing ourself right out of a job—or maybe a couple of jobs.

If this is true it strikes at the very democratic basis of our science and we are in danger of having the FBI on our trail. However, like all generalizations, it is probably partly true and partly false, but wholly worth thinking about.

We proceed with our teaching of science somehow on the assumption that we are going to reduce material phenomena to *simpler* terms by means of experiment, demonstrations, and clever analogies. But sooner or later we discover that nature just *isn't* simple; the further we go the more complicated it becomes. If you think this is discouraging, science is not for you. Some of us find it as stimulating as opening up new, unexplored territories.

Chemistry shares with physics our body of knowledge about the behavior of matter. Chemistry cannot get very far in the explanation of material behavior without the help of physics, and look at the fix physics is in! Most of us find it impossible to think concretely except in terms of conventional mechanical similes, and we are given to understand that matter just doesn't work that way. Not that a satisfactory basis *can't* be laid, but most of us are too old or too inflexible to lay it. And that is just the point; perhaps we can't all of us aspire to know what it is all about.

The clue to chemical behavior and the properties of matter is in the structure and internal mechanism of the atom. In the last analysis, the measure of our understanding of the former is in the clearness of our knowledge of the latter. And the gospel of subatomics is scarcely a thing to be spread to the multitude, widely.

Must chemistry, therefore, inevitably become esoteric? Must chemists become a priesthood, set apart? It probably all depends upon where we choose to draw lines and make definitions; what "degrees of initiation" we establish. The fact that an enormous body of knowledge is now the possession of the many does not preclude the existence of fields into which only the select may venture. Wisdom will probably always be hierarchical.

All this simply gets us into the general philosophy of education and the dissemination of knowledge. Our system must assure to everyone the opportunity to learn as fast and as much as his limitations will permit. If this stops him short of what we choose to call "chemistry" he will be ignorant of it. In which case, probably most of us will.

Meanwhile, the field of chemical education will remain just where it was, concerned mostly with a wider, if not deeper, popular comprehension of the material changes that make life more comfortable and interesting.

Perhaps we shouldn't have brought up this question. But, anyway, chemistry *is* becoming darned complicated and difficult to understand.

DURING the last few months a large portion of our correspondence column has been devoted to the discussion of the relative merits of this or that particular designation for the so-called "atomic weight unit." There is no doubt that we can talk more definitely about a thing when we can give it a name. Each of us turns more quickly at the sound of his own name than to an impersonal "Hey, you!" But a vague feeling seems to crop up that atomic weights are in some way different from other weights because they involve the idea of *proportion*. We emphasize needlessly the point that the weight of the carbon atom is twelve *times* the weight of the hydrogen atom (or nearly), as though that weren't true of any scale of weights. You weigh seventy *kilograms* (or do you?) because you weigh seventy *times* the weight of a chunk of platinum stored away in Paris (or at least we hope it is still there!). When it comes to atomic weights, we need not—and could not—store away infinitesimal standards, but fortunately we have satisfactory standards flying about us all the time in the oxygen atoms of the air, and we can simply reach out and collect a few whenever we need them. This tends to make our scale of atomic weights less arbitrary than most weight scales, for the standard of comparison is a reproducible one which exists in nature. It is, of course, an old story that the metric scale was also *intended* to be reproducible, based upon natural properties and constants, but that the desirability of translating these into tangible weights and measures necessarily led to inaccuracy and an eventual arbitrary scale. This outcome has its analogy, of course, in the field of atomic weights in the fact that the weights of all oxygen atoms are not the same and that we will have a slightly different weight standard if we compare with individual atoms rather than statistically, with a large number. As a pedagogical problem, however, the future will doubtless see more and more emphasis placed upon the determination of atomic weights by the "physical method," which is perfectly direct and understandable and which will tend to clear up some of the vagueness surrounding the idea of equivalent weights of elements.

What's Been Going On

In the Field of Fiber Chemistry

ACCORDING to D. H. Powers, of Röhm and Haas Company, Inc., "recent years have seen the development of clear colorless synthetic resins for textile fabric modification. These resins are applied as aqueous solutions or dispersions. In contrast to the older textile-coating resins for producing artificial leather and similar types of coated fabrics, these impregnating resins do not alter the surface appearance. However, they may greatly improve the textile strength, resilience, durability, luster, and firmness of the fabrics. They impart to vegetable fibers many of the properties of animal fibers . . . . The use of these water-dispersed synthetic resins is of increasing value and importance in the development of new and unique textile and industrial fabrics."

The urea-formaldehyde and the acrylate resins, both of which are clear and easily applied, are most generally used in coating fabrics. Certain specific effects are obtained by the use of the alkyd, the vinyl, or the styrene resins, which accounts for a gradual increase in their use.

Prolon is the name suggested by F. C. Atwood, of Atlantic Research Associates, Inc., for natural protein-base spun fibers. One of these products, lanital, has properties much more like those of wool than those of rayon or other synthetic fibers. Although prolon has not attained commercial production in the United States, factories produce this type of fiber commercially under the names of cargan in Belgium, Casolana in Holland, Courtaulds casein in England, lanital in Italy, Polan in Poland, and Tiolan in Germany. It begins to look as though the sheep, as the silkworm has already done, may give way to spinnerettes.

The soybean protein fiber, as produced at present, according to R. A. Boyer of the Ford Motor Company, has "about 80 per cent of the strength of wool, has more elongation both wet and dry, and does not wet so easily as wool or casein fiber." It does not promote mold, blends well with both wool and cotton, and may be processed satisfactorily. A pilot plant that will process 1000 pounds of soybean fiber a day is in the offing.

The electrocoated pile fabrics, according to N. E. Oglesby and L. E. Hoogstoel of Behr-Manning Corporation, represent an outgrowth of the development of electrocoated sandpaper. The two important types of textiles now being produced commercially by the electrostatic process are "women's dress goods decorated with a pile design, and an all-over covered pile product for such service as car interiors and upholstery." The success of the process is dependent upon accurate control with respect to the length of the pile, the type of adhesive, and the humidity conditions of manufacture. "The outstanding feature of a pile fabric manufactured by the electrostatic process is the density of the pile attainable, which reflects in the wearing properties of the product so made. As high as 275,000 fibers per square inch are obtained."

The cellulose acetate rayons, according to H. D. Smith of the A. M. Tenney Associates, Inc., account for about 30 per cent of the total rayon production. The acetate rayon filaments and fibers are produced by extruding an acetone solution of cellulose acetate through spinnerettes, countercurrent to warm air under carefully controlled conditions of humidity, temperature, velocity, and tension during the period of coagulation. The conditions of spinning determine the diameter and the physical properties of the fiber, whereas the color and luster are varied by the addition of dyes and pigments. The acetate rayons are obtained both as continuous filaments for the fabric trade and as acetate rayon staple (short) fibers for processing into yarns similar to those of cotton and wool. The acetate rayons compare in strength with that of wool, are white with a good resistance to creasing, have a "soft supple nature," and are subject to cross-dyeing. Chemically, the acetate rayons are acetylated-cellulose molecules, which are extruded in solution under conditions that impart strong intermolecular physical bonds.

Nylon, according to G. P. Hoff of E. I. du Pont de Nemours and Company, is "the generic name for all synthetic fiberforming polymeric amides having a protein-like chemical structure, derivable from coal, air, and water or other substances and characterized by extreme toughness and strength." By virtue of the peptide linkage in the nylon molecule, it is related chemically to such protein fibers as silk and wool. The latter have the general molecular configuration of

$$RH(NH_2)C\cdot CO\cdot(NH\cdot CHR\cdot CO\cdot NH\cdot CHR\cdot CO\cdot NH\cdot CHR\cdot CO)_n\cdot NH\cdot CHR\cdot CO_2H,$$

whereas that for nylon is best represented by:

$$[\cdot CO\cdot(CH_2)_n\cdot CO\cdot NH\cdot(CH_2)_n\cdot NH]_n$$

Under standard elasticity tests, "nylon showed 100 per cent recovery in comparison with 50 for natural silk, 50 for acetate rayon, 40 for Cordura rayon, and 30 for ordinary viscose yarn." The melt-extruded filaments of nylon may be stretched to produce orientation, which results in the formation of an elastic, but tough and strong, filament. Nylon is non-flammable, is physiologically inert, and is resistant to enzymes, mildew, molds, and moths.

Vinyon, according to F. Bonnet of American Viscose Corporation, "is a copolymerized vinyl resin made of vinyl chloride and vinyl acetate." The polymerization is of the additive type at the unsaturated linkages to give a continuous chain molecule, which is characteristic of the fiber materials. The stability of the fiber is increased by the plasticizing action of the vinyl acetate on the copolymer. The product is dissolved in acetone and extruded through spinnerettes, countercurrent to warm air under carefully controlled conditions. Although the spun yarn is not strong, the orientation of the molecules under tension increases the tensile strength of the filaments to values as high as 80,000 pounds per square inch. The yarn is resistant to water, acids, alkalies, and shows little or no decrease in strength on wetting. Vinyon is readily dyed, and is thermoplastic, but undergoes shrinkage if heated above 60°C. One of the largest uses at present is in the production of industrial filter cloth, but the remarkable properties of vinyon lend it to many other uses.

Fiberglas, according to G. Slater of the Owens-Corning Fiberglas Corporation, "possesses desirable properties not found in any other commercially available material." This product is obtained as wool-like fibers for insulation, and as continuous and staple-length fibers for the textile trade. These glass fibers have a distinct advantage over ordinary synthetic and natural fibers in that they are inorganic, incombustible, non-absorptive and have excellent tensile strength, electrical properties, and heat resistance. They are not attacked by ordinary chemicals, nor are they preyed upon by fungus growths or vermin. The fiberglas may be colored by use of minerals, in which event the hues are sun-fast and durable, or the use of dyes for surface coloring may be employed. The wool forms of fiberglas are used extensively for the insulation of aircraft, houses, ranges, refrigerators, ships, and trains, and for industrial insulations between 0° and 1000°F. The textile forms are used in electrical insulation, in battery retainer mats, and in chemical and fume filtration. Decorative fabrics of this group are finding many practical applications, but the fiberglas fabrics are not recommended for wearing apparel.

Ethyl cellulose is now being produced on an experimental basis by treating sodium cellulose with ethyl chloride. When the ethyl cellulose is dissolved in a suitable solvent and extruded through spinnerettes, filaments are obtained which are superior in some respects to those obtained from cellulose acetate. Ethyl cellulose is more resistant to the action of alkalies than is cellulose acetate, hence undergoes deterioration much less rapidly by

(*Continued on page 226.*)

Eminent Men of Science Living in 1807–8[1]

H. MONMOUTH SMITH *Brookline, Massachusetts*

INVENTORS and engineers were in the majority among the eminent men of science living in 1807–8.

James Watt (1736–1819) made the most fundamental contributions to the steam engine. He employed valves to make the engine double acting, and obtained rotary motion by the use of the fly-wheel and crank; he also used a separate condenser into which steam expanded. William Symington (1763–1831) invented a steam engine using a piston connected to a crank on the paddle shaft. In 1788 Symington and Patrick Miller (1730–1815), who was the first successfully to propel vessels by paddle wheels moved by manual labor, made a satisfactory demonstration of steam applied to paddle wheels, the boat proceeding at a speed of six miles per hour. The *Charlotte Dundas*, the first practical steam boat, towed two laden vessels of 70 tons in March, 1803. Thomas Cochrane, Earl of Dundonald (1775–1860), applied the screw propeller to warships and early saw the advantage of steam power for the navy. Henry Maudslay (1771–1831), an engineer, invented the marine engine, boiler-feed machinery, a screw cutting lathe, and machines registering to one ten-thousandth of an inch. Sir Samuel Bentham (1757–1831), naval architect and engineer, invented machines for planing, sawing, and boring both wood and metal, and also a dovetailing machine. He introduced many mechanical devices into ships. Thomas Telford (1757–1834), civil engineer, constructed the Caledonian Canal and over 1000 miles of highway and 1200 bridges. His name is retained in the Telford type of crushed stone road construction. William Jessop (1745–1814) built many canals which opened up the English coal fields to the manufacturing parts of the country; the canal system of England is largely due to his engineering ability. Jessop originated the flood-storage system to supply his canals. John Rennie (1761–1821) constructed the East India and many other docks, as well as the Portsmouth and Plymouth naval ports. Joseph Huddart (1741–1816) made

[1] The brief biographies in this article are summarized from an early publication: "Memoirs of the distinguished men of science of Great Britain living in the years 1807–1808," with an introduction by SIR ROBERT HUNT, F.R.S., compiled and arranged by WILLIAM WALKER, JR., 2nd ed., London, **1864**. The portraits of the men discussed may be found in the frontispiece, to which the accompanying outline key is given.

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5—Dollond	15—Wollaston	25—Congreve	35—Maskelyne	45—Tennant
6—Young	16—Hatchett	26—Donkin	36—Jenner	46—Cartwright
7—Brown	17—Davy	27—Fourdrinier	37—Cavendish	47—Ronalds
8—Gilbert	18—Maudslay	28—Thomson	38—Dalton	48—Stanhope
9—Banks	19—Bentham	29—Symington	39—Brunel	
10—Kater	20—Rumford	30—Miller	40—Boulton	

surveys of many ports and constructed charts of many coasts in his service for the East India Company. Charles Mahon Stanhope (1753–1816), associated with Robert Fulton in the application of steam to navigation, also devised the Stanhope printing press, calculating machines, and fireproofing processes. Bryan Donkin (1768–1855) invented printing machinery using two colors; and also worked on dividing, screw cutting, and paper-making machinery. Henry Fourdrinier (1766–1854) perfected the continuous paper-making machine. Sir Marc Isambard Brunel (1769–1849), architect, inventor, and engineer, improved shoe and knitting machinery, introduced stereotype plates in printing, built the floating landing piers in Liverpool, constructed the Thames tunnel, and invented the "shield" employed in this work. Samuel Crompton (1753–1827) invented the spinning-mule, and in so doing conferred a great benefit upon his country, while reaping little profit for himself. Edmund Cartwright (1743–1823) was a clergyman who became interested in machinery and invented the first power loom and wool-carding machine. Sir Francis Ronalds (1788–1873), inventor of the electric telegraph, was Director of the Meteorological Observatory at Kew, where he installed many continuous automatic registering instruments of his own invention. Joseph Bramah (1749–1814) is known for his mechanical inventions in pumps, fire engines, and printing presses. A hydrostatic press is known by his name. In the engraving, Bramah's back is turned, since no portrait of the man existed, and the engraver evidently did not wish to draw upon his imagination. Richard Trevithick (1771–1833) developed the locomotive engine by coupling together the locomotive wheels, thus obtaining the necessary traction, making it possible to discard the rack and pinion. In 1804 the first successful railway locomotive had a horizontal cylinder, cranked axle, fly-wheel, safety valve, and two piston rods set at quarter turns. Edward Charles Howard (1774–1816) invented the vacuum pan for the refining of sugar. Sir William Congreve (1772–1828), an army engineer, invented the artillery rocket.

Industrialists, putting the multitudinous inventions of the time into production, counted among them William Murdock (1754–1839), the first to show the practical use of coal gas for illuminating purposes by lighting his own home (1792) with gas produced in an iron retort. Murdock received the Rumford Medal for lighting the Manchester mills. Westminster Bridge was lighted in 1813, Paris streets in 1820. Baltimore was the first city in the United States to use it (1816), followed by Boston in 1822 and New York in 1823. Murdock made improvements in Watt's steam engine, invented the double slide valve, and experimented with high-pressure locomotives. Matthew Boulton (1728–1809) founded the great Soho steel plant, and was a partner with James Watt in the manufacture of steam engines. Boulton recoined the whole British specie and directed the arrangement of the machinery for the British mint. Charles Tennant (1768–1838) introduced the use of chloride of lime in the bleaching of cotton cloth, thus replacing the slow sunlight method. He founded a chemical works for the manufacture of saturated chloride of lime, which displaced the more expensive "*eau de Javelle*."

Chemists, physicists, astronomers, mathematicians, and naturalists were also prominent in the world of 1807–8. Sir Humphry Davy (1778–1829), who discovered the effects of laughing gas, was appointed lecturer at the Royal Institution at the age of 22. He isolated sodium, potassium, barium, strontium, and magnesium, and showed the elementary nature of chlorine and iodine and the composition of hydrochloric acid. He is also known as the inventor of the miner's safety lamp. Henry Cavendish (1731–1810) was a wealthy recluse who devoted his time and means to the sciences. Although known for his recognition of the elementary nature of hydrogen and his synthesis of water, he contributed to the knowledge of the properties of carbon dioxide, the specific heats of substances, the heats evolved in the solidification of liquids, and the density of the earth. He was an independent discoverer of nitrogen and predicted the discovery of argon. He was also first to introduce a method for drying gases and storing them over mercury. He founded the Cavendish Laboratory at Cambridge. The engraver has made use of the Alexander drawing of Cavendish, sketched at a dinner unbeknown to Cavendish—the only authentic likeness of him in existence. John Dalton (1766–1844) developed the atomic theory and the Law of Multiple Proportions. His other fields of study lay in the composition of mixed gases, known as Dalton's Law of Partial Pressures, the expansion of gases by heat, and the absorption of gases by water. Daniel Rutherford (1749–1819) discovered nitrogen. William Hyde Wollaston (1766–1828) discovered palladium and rhodium and developed a method for making platinum malleable. First to note the dark lines in the sun's spectrum, later rediscovered by Fraunhofer, Wollaston also invented the reflecting goniometer. Charles Hatchett (1765–1847) discovered the element columbium in 1801 in a specimen of rock sent by Governor John Winthrop, of Connecticut, to Sir Hans Sloane (1660–1753). The specimen of rock came from near Winthrop's home in New London, Connecticut, and had been deposited in the British Museum by Sir Hans. William Allen (1770–1843) determined the proportion of carbon in carbon dioxide, showed the chemical identity of diamond and charcoal, and was active in all movements to advance philanthropic, educational, and economic conditions. Thomas Thomson (1773–1852), professor of chemistry at Glasgow, introduced laboratory instruction in chemistry into England, and founded and edited "Annals of Philosophy."

One of the more notable of the physicists, Benjamin Thompson, Count Rumford (1753–1814), founder of the Royal Institution, was born in North Woburn, Massachusetts, near Boston. He was knighted by George III and made Count of the Holy Roman Empire by Maximilian I. While directing the boring of cannon

for the Bavarian army, Count Rumford discovered the relation between heat and work and announced that heat was "not a fluid but a mode of motion." He studied the expansion of water and ice; improved the construction of fireplaces and the preparation of food. Rumford married Lavoisier's widow. He left bequests to Harvard University, the American Academy of Arts and Sciences, and the Royal Society of London. Thomas Young (1773–1829) was the first to describe and measure astigmatism. He explained color blindness and proposed the theory of the interference of light. Helmholtz regarded him as "one of the most clear-sighted men who ever lived." William Henry (1774–1836) formulated the gas law known as Henry's Law. Henry Kater (1777–1835) determined the length of the seconds pendulum for the latitude of London. He invented various physical instruments, including the floating collimator; he improved the needle of the mariner's compass. Sir John Leslie (1766–1832), a professor at Edinburgh, invented a differential thermometer, produced cold by use of the air pump, and froze mercury.

Francis Baily (1774–1844), astronomer, founder of the Astronomical Society, studied the earth's ellipticity, seconds pendulum, and density of the earth. "Baily's Beads," a phenomenon of the sun's eclipse, was first observed by him. Sir William Herschel (1738–1822) constructed his own telescope, discovered the planet Uranus and six of its satellites and also two of Saturn's. From his start as a music teacher he became Astronomer Royal. Peter Dollond (1730–1820) reduced the spherical error of the telescope by the use of triple achromatic object glasses. Nevil Maskelyne (1732–1811), an astronomer, director of the Greenwich observatory, founded the Nautical Almanac and published the British Mariner's Guide.

Mathematicians were John Playfair (1748–1819) and Davies Giddy Gilbert (1767–1839), member of the Board of Longitude, who revised the British weights and measures.

Representing the field of medicine was Edward Jenner (1749–1823) who discovered the prophylactic power of vaccination. He inoculated his son with swine-pox, and found that he then became immune to smallpox.

Robert Brown (1773–1858) was a Scottish botanist who studied the flora of Australia. He discovered the movements of minute particles suspended in water, known as the "Brownian movements." Sir Joseph Banks (1743–1820) was a naturalist who accompanied Cook's expedition around the world. His collections are preserved in the British Museum.

An architect of the time was Robert Mylne (1753–1811), who constructed the Blackfriars Bridge and many large buildings. Contrary to the usual type of eminent man pictured, Alexander Nasmyth (1758–1840) was a portrait and landscape painter.

These men were the pioneers in the application of Power to man's daily work. The locomotive, the steam engine, the power loom, and the new modes of transportation were destined to bring changes in English life—changes which left many a Sweet Auburn to wither while other communities became large and prosperous industrial centers. These changes affected not only England but the entire civilized world. Though some of our present-day ills may be traced to this period, certainly most of our present-day comforts and freedom from drudgery found their origin in the work of this group of men.

Editor's Note:

Further references to these men may be found in the JOURNAL OF CHEMICAL EDUCATION as follows:

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(*Continued on page 226.*)

A Résumé of the Proton Transfer Concept of Acids and Bases

HUBERT N. ALYEA *Princeton University, Princeton, New Jersey*

THE acceptance of the proton transfer concept of acids and bases in the general chemistry course awaits a more extensive discussion in the textbooks. To further its adoption this outline is presented, so that the teacher may organize and amplify the material to suit his own class needs. The nomenclature adheres strictly to that previously suggested (*1*).

TRANSFER OF ELECTRONS AND OF PROTONS

Reducing agents have the chemical property of losing *electrons;* oxidizing agents have the property of accepting *electrons.*

$$Fe^0 + Cu^{+2}SO_4 \longrightarrow Cu^0 + Fe^{+2}SO_4$$
$$\searrow 2\epsilon \nearrow$$

Fe is the reducing agent; it loses electrons to copper. This reaction involves a transfer of electrons, and is called an oxidation-reduction reaction.

There is another class of substances which has the chemical property of losing or accepting *protons* (H^+); these substances are called *acids* and *bases.* In the following reaction HCl acts as an acid, H_2O as a base:

$$HCl + H_2O \rightleftarrows H_3O^+ + Cl^-$$
$$\searrow H^+ \nearrow$$

Stated formally, if the reaction

$$A \rightleftarrows H^+ + B$$

can occur at all, A may be called the *conjugate acid,* whatever its charge, and B may be called the *conjugate base,* irrespective of the actual stoichiometrical course of the reaction. Together they form a *conjugate pair.* In the above reaction HCl and Cl^- form one conjugate pair, H_3O^+ and H_2O form another. A number of conjugate pairs are given in Table 2, where it will be noticed that acids include not only *neutral molecule acids* (HCl, H_2SO_4, HNO_3), but also *cation acids*

TABLE 1

PROTOLYTIC REACTIONS

	A_1		B_2		A_2		B_1
General Form for a Protolytic Reaction							
Ionization is a protolytic reaction between a molecule	HCl	+	H_2O solvent	⇄	H_3O^+	+	Cl^-
and its solvent resulting in the formation of ions	H_2O solvent	+	NH_3	⇄	NH_4^+	+	OH^-
Neutralization is any protolytic reaction. Often, not always, it was identified with titration to an endpoint, where approximately equivalent quantities of acid and base are mixed (equations 1, 3, 4, 6, 7)							
It may be salt destroying	$H_3O^+Cl^-$ a salt	+	K^+OH^- a salt	⇄	$2H_2O$	+	K^+Cl^- a salt
—is not necessarily salt destroying	HCl	+	H_2O	⇄	H_3O^+	+	Cl^- a salt
—does not necessarily involve water	HCl	+	CH_3COONa	⇄	CH_3COOH	+	NaCl (in CH_3COOH)
	HCl	+	NaOH	⇄	HOH	+	NaCl (in water)
—is not restricted to neutral molecule acid-base reactions	H_3O^+	+	CH_3COO^-	⇄	CH_3COOH	+	H_2O
The old definition of neutralization is represented by the reaction	HX neutral molecule acid	+	M^+OH^- metallic hydroxide	⇄	H_2O water	+	M^+X^- a salt
Heat of neutralization in aqueous solution is given by	H_3O^+	+	OH^-	⇄	$2H_2O$	+	13,780 cals.
Formation of salts, pseudo-salts, and esters							
—is not restricted to neutral molecule acids and bases	H_3O^+	+	CH_3COO^-	⇄	CH_3COOH	+	H_2O
—is not always accompanied by the liberation of water	CH_3COOH	+	C_2H_5COONa	⇄	C_2H_5COOH	+	CH_3COONa
Addition reactions are often protolytic reactions	HCl	+	NH_3	⇄	NH_4^+	+	Cl^-
Leveling effect of water is a protolytic reaction between							
—strong acids and water to form the hydronium ion, the presence of which gives an appearance of equal strengths to acids whose strengths differ in non-aqueous solvents	HCl	+	H_2O	⇄	H_3O^+	+	Cl^-
	HNO_3	+	H_2O	⇄	H_3O^+	+	NO_3^-
—strong bases and water to form the hydroxyl ion, etc.	H_2O	+	KNH_2	⇄	NH_3	+	K^+OH^-
	H_2O	+	K_2O	⇄	$2K^+OH^-$		
Displacement of a weak acid by a strong one is useful in preparing salts of strong acids	HNO_3	+	CH_3COO^-	⇄	CH_3COOH	+	NO_3^-
Lyolysis (*hydrolysis, ammonolysis*) is a protolytic reaction between a cation acid or an anion base and the solvent	$NH_4^+Cl^-$	+	H_2O solvent	⇄	$H_3O^+Cl^-$	+	NH_3
	H_2O solvent	+	$CH_3COO^-Na^+$	⇄	CH_3COOH	+	Na^+OH^-
Protolytic catalysis is a catalysis in which acids, bases, or both act as catalysts by undergoing protolytic reactions. Mutarotation of sugar, SH to HS, is an example of acid-base protolytic catalysis	$A_1 + SH + B_2 \rightleftarrows A_2 + HS + B_1$						

(NH_4^+, H_3O^+) and *anion acids* (HSO_4^-, $H_2PO_4^-$); and bases are similarly represented. The new concept of acids and bases assumes that $O^=$ and OH^- are bases, while hydroxides which furnish OH^- in water solution are not bases but salts. Any ionic substance is a *salt;* and this includes substances such as NaOH and CaO.

PROTOLYTIC REACTIONS

Corresponding to oxidation-reduction reactions, which involve *transfer of electrons*, we have protolytic reactions which involve *transfer of a proton* from an acid to a base. Table 1 shows that a great many common reactions are really protolytic reactions.

PROTOLYTIC CATALYSIS

The greatest achievement of Brønsted and his coworkers in applying this proton transfer concept has been in the field of catalysis in aqueous and non-aqueous solvents. Much of this material is beyond the scope of the general chemistry course, and is therefore merely summarized.

Acid catalysts include H_3O^+ and NH_4^+ [Hammett (*2*), Brønsted (*3*)]. *Basic catalysts* include $SO_4^=$, Werner complexes such as $Co(NH_3)_5OH^{++}$, and NH_3, studied in the decomposition of nitramide [Brønsted (*3*), Livingston (*4*)]. The mutarotation of glucose in both non-aqueous solvents and in water is an example in which acid and basic catalysts must be simultaneously present [Lowry (*5*), Brønsted (*3*)]. Lowry also presents a mechanism for this particular reaction.

There are two types of protolytic catalysis, *specific and general.* Pedersen (*6*) gives a derivation showing how general acid catalysis may become specific. In addition there are so-called *primary and secondary salt effects* [Brønsted (*3*), Livingston (*4*)].

STRENGTHS OF ACIDS AND BASES

The electromotive force series indicates the ease with which an element loses electrons. It predicts, for example, that iron will displace copper in a solution of copper sulfate.

Analogously a scale of the relative strengths of acids and bases predicts the probable occurrence of a protolytic reaction. The relative strengths of acids measures the extent of reaction of the acids with a given base under identical conditions; the stronger acid reacts more completely.

A. Measuring the Strengths of Acids and Bases.— Unfortunately no absolute scale of acid and base strengths exists, for the solvent employed must always be taken into consideration. Substance A_1 may be a stronger acid than A_2 in one solvent, and a weaker acid in another solvent, for different solvents act differently upon acid and base ions of different charges. Brønsted (*3*), Conant (*7*), and Hall (*8*) give tables illustrating this influence of solvent and charge. Kolthoff (*9*) demonstrates mathematically that the ionization constants in water do not measure true acidity in other solvents.

As long as the discussion is limited to *aqueous* solutions, however, the ionization constant of the acid may be taken as an index of its strength. The lower the pH of a solution containing equal concentrations of an acid and its conjugate base, the stronger the acid and the weaker its conjugate base.

Thus in the two protolytic reactions

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

the latter reaction proceeds so slightly to the right that the concentration of H_3O^+ is small indeed. The pH will be greater for acetic than for hydrochloric acid; we say that the acid strength of HCl is greater than the acid strength of CH_3COOH.

In place of pH as a measure of strength it is more convenient to use pK (pronounced pee-kay), the ionization constant or protolysis constant. That we may do this, *i. e.*, that pK = pH for a solution containing equivalent quantities of acid and base, is shown by the following considerations. For the equilibrium

$$A + H_2O \rightleftharpoons H_3O^+ + B$$

the ionization constant, taking C_{H_2O} as constant, is given by

$$K = \frac{[C_{H_3O^+}][C_B]}{[C_A]}$$

from which we see that when $C_A = C_B$ we have

$$K = C_{H_3O^+}$$

$$-\log_{10}K = -\log_{10}C_{H_3O^+}$$

$$pK = pH$$

The strengths of bases may be experimentally determined by titrations with base indicators [Hammett (*2, 10*), Kilpatrick (*11*)].

The strength exponents of some conjugate pairs are given in Table 2.

TABLE 2

STRENGTH EXPONENTS OF SOME CONJUGATE PAIRS

Conjugate Acid	*Conjugate Base*	*Strength Exponent* pK
HCl (*strong*)	Cl^- (*weak*)	~ −7
H_2SO_4	HSO_4^-	Negative
HNO_3	NO_3	Negative
H_3O^+	H_2O	− 1.74
HSO_4^-	SO_4^{--}	+ 1.70
H_2SO_3	HSO_3^-	1.77
H_3PO_4	$H_2PO_4^-$	2.12
$Fe(H_2O)_6^{+++}$	$Fe(H_2O)_5OH^{++}$	2.20
HCH_3COO	CH_3COO^-	4.75
$Al(H_2O)_6^{+++}$	$Al(H_2O)_5OH^{++}$	4.90
HSO_3^-	SO_3^{--}	5.30
H_2CO_3 or CO_2	HCO_3^-	6.51
H_2S	HS^-	7.10
$H_2PO_4^-$	HPO_4^{--}	7.23
HClO	ClO^-	8.00
HCN	CN^-	9.20
H_3BO_3	$H_2BO_3^-$	9 20
NH_4^+	NH_3	9.26
HCO_3^-	CO_3^{--}	10.34
H_2O_2	HO_2^-	11.70
HPO_4^{--}	PO_4^{---}	12.46
HS^-	S^{--}	14.70
H_2O	OH^-	15.97
OH^- (*weak*)	O^{--} (*strong*)	~24

B. Protolysis Equilibrium Determined by pK.—As intimated above, pK may be used to predict the extent of proton transfer in the same way that in oxidation-reduction reactions the electromotive force may be used to predict electron transfer. For if in the protolytic reaction

$$A_1 + B_2 \rightleftharpoons A_2 + B_1$$

the tendency for the acid A_1 to lose its proton to B_2 is stronger than it is for A_2 to lose its proton to B_1, the reaction proceeds more to the right. This occurs when strength $A_1 \gg$ strength A_2; that is, when $pK_{A_1} \ll pK_{A_2}$. Generalizing these conditions we may state that *any acid in Table 2 will react more or less completely with any base below it in the table, but will react only slightly, if at all, with any base above it in the table.* In the following examples the acids are underlined:

Ionization
- complete $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$
- slight $\underline{H_2O} + NH_3 \rightleftharpoons \underline{NH_4^+} + OH^-$
- very slight $\underline{2H_2O} \rightleftharpoons \underline{H_3O^+} + \overline{OH^-}$

Neutralization
- complete $\underline{H_3O^+} + \overline{OH^-} \rightleftharpoons 2H_2O$
- complete $\underline{CH_3COOH} + \overline{OH^-} \rightleftharpoons \underline{H_2O} + \overline{CH_3COO^-}$
- very slight $\underline{CH_3COOH} + Na^+ Cl^- \rightleftharpoons \underline{HCl} + \overline{CH_3COO^- Na^+}$

Hydrolysis
- slight $\underline{NH_4^+}Cl^- + H_2O \rightleftharpoons \underline{H_3O^+} + Cl^- + NH_3$
- slight $\underline{H_2O} + K^+\underline{CN^-} \rightleftharpoons \underline{HCN} + K^+ OH^-$

Leveling effect of water
- complete $\underline{HCl} + H_2O \rightleftharpoons \underline{H_3O^+} + Cl^-$

C. pH of a Salt Determined by pK.—The relative acid and base strengths of its constituent ions determine the pH of a salt. The cases which follow should be checked against the pK values in Table 2. This simple scheme replaces the cumbersome hydrolysis equilibria usually presented in general chemistry to show why salts such as KCN, $FeCl_3$, and Na_2S do not react neutral to litmus.

Case 1—*Na^+, K^+, Ca^{++}, Ba^{++} and Mg^{++} all behave as very weak acids; hence the pH of their salts is determined by the nature of the anion present.*
- —the salt gives a *neutral* reaction to litmus if the anion is a very weak base, *viz.*, NaCl, KNO_3, $BaCl_2$, $MgSO_4$.
- —the salt gives a *basic* reaction to litmus if (*a*) the anion can be only a base, *viz.*, CaO, Na_2S, K_3PO_4, KCN, $BaCO_3$ or (*b*) the anion is stronger as a base than as an acid, *viz.*, $NaHPO_4$, KSH, $Ca(HCO_3)_2$.
- —the salt gives an *acid* reaction to litmus if the anion is stronger as an acid than as a base, *viz.*, $NaHSO_4$, $KHSO_3$, NaH_2PO_4.

Case 2—*A salt gives an acid reaction to litmus* if it contains an *acid ion* which is stronger than the base ion, *viz.*, H_3OCl, NH_4Cl, $Al(H_2O)_6Cl_3$, and NH_4HSO_4.

Case 3—*A salt gives a basic reaction to litmus* if it contains a *basic ion* which is stronger than the acid ion, *viz.*, $(NH_4)_2S$, $Fe(H_2O)_6(OH)_3$, and $Al(H_2O)_5(OH)Cl_2$.

Case 4—*A salt gives a neutral reaction to litmus* if its acid and base ions are of approximately equal strength, *viz.*, NH_4CH_3COO, $Al(H_2O)_6PO_4$, and NH_4HSO_3.

D. pH of Buffer Solutions Determined by pK.—This topic is usually omitted in the general chemistry course. Excellent elementary treatment is given, however, by Kilpatrick (*11*). Bjerrum (*12*) shows that the acid-base ratio in a solution containing a conjugate pair can be varied widely without changing the pH appreciably.

INDICATORS

An *indicator* is any conjugate pair in which the conjugate acid differs in color from its conjugate base. Thus litmus changes color at pH 7, corresponding to its strength exponent pK, according to the protolytic equilibrium:

$$\underset{\text{(red)}}{H^+\cdot\text{litmus}} + H_2O \rightleftharpoons H_3O^+ + \underset{\text{(blue)}}{\text{litmus}}$$

For titration data in non-aqueous as well as aqueous solutions see Hammett (*2*), LaMer (*13*), and Bjerrum (*14*); also the excellent laboratory experiments by Flowers (*15*).

PREPARATION OF PURE SALTS

The preparation of pure salts by the reaction

$$A_1 + B_2 \rightleftharpoons A_2 + B_1$$

is considerably simplified if B_2 is a salt containing the *lyate ion* (a solvent molecule minus a proton). Thus in the preparation of lithium chloride in water solution we might

(1) use the lyate ion $HCl + LiOH \longrightarrow LiCl + H_2O$ in water
(2) not use the lyate ion
$HCl + CH_3COOLi \longrightarrow LiCl + CH_3COOH$ in water.

Obviously (2) would be more difficult to purify since both water and acetic acid must be removed from the lithium chloride.

On the other hand, lithium chloride might be simply prepared in solvents other than water by employing the lithium lyate for B_2 in each case; *viz.*,

$HCl + LiOH \longrightarrow LiCl + H_2O$ in water
$HCl + LiNH_2 \longrightarrow LiCl + NH_3$ in liquid ammonia
$HCl + \underset{\text{lithium lyate}}{CH_3COOLi} \longrightarrow LiCl + \underset{\text{solvent is formed}}{CH_3COOH}$ in glacial acetic acid

VALUE OF PROTON TRANSFER CONCEPT OF ACIDS AND BASES

This résumé emphasizes the advantages of redefining acid and base in terms of this Brønsted concept of proton transfer. It de-emphasizes the importance of OH^- and H^+, and recalls that reactions may be carried out in non-aqueous solvents as well as in water [Brønsted (*3*), Kilpatrick (*16*), Hantzsch (*17*), Flowers (*15*)]. For example, there is not merely a systematic comparison of H_2O and CH_3COOH, but rather there is an actual decrease in hydrogen ion activity when the base CH_3COO(Na) is dissolved in CH_3COOH just as when the base (Na)OH is dissolved in H_2O. Moreover, protolytic catalysis, which is of growing industrial importance in non-aqueous solvents [Hall (*8*)] as well as in water, is not always a hydrogen ion catalysis [Brønsted (*3*), Hammett (*17*), Kilpatrick (*16*), Livingston (*4*)]. These concepts explain why acid-base indicators change color in non-aqueous, low-conductivity media [LaMer (*13*)]; why covalent methyl

iodide reacts with silver nitrate as rapidly in alcohol as in water [Noyes (*18*)]; and why HCl and H_2O do not conduct until mixed [Brønsted (*19*), Lowry (*20*)]. The physiological chemistry of lipoid phases is possible only under the new system [Hall (*8*)]. Water is not neutral but amphiprotic [Brønsted (*19*)]. There is no correlation between thermodynamic properties (*e. g.*, freezing point lowering, electromotive force, or indicator changes which represent equilibrium states) on the one hand, and irreversible, non-thermodynamic reactions (*e. g.*, conductivity, OH^- and H^+ catalysis) on the other [LaMer (*13*)]. Hydrolysis, a bugbear for the beginner, is explained simply. The formal analogy of electron transfer (oxidation-reduction) to proton transfer (acid-base) is attractive [Hall (*8*), Schwarzenbach (*21*)]. In fact the whole concept of proton transfer is attractive, and should soon find its way into the general chemistry textbook (*22*).

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(22) Teachers of organic chemistry should welcome the lucid presentation of the Lewis Electronic Theory of Acids and Bases by LUDER in *Chem. Rev.* **27**, 547 (1940). On the other hand, the limited treatment of acids and bases in the general chemistry course is probably more easily handled by the less generalized system of proton transfer reviewed above.

COURSES FOR TEACHERS IN THE PHYSICAL SCIENCES AT THE UNIVERSITY OF CHICAGO

DURING the Summer Quarter the University of Chicago is offering two courses for persons interested in the teaching of integrated courses in the physical sciences at the senior high school and junior college levels. These courses acquaint teachers with the subject matter of an integrated course, its organization, and methods of presentation. They are accepted for professional requirements (education) and for the Divisional Master's degree in the Physical Sciences. The material will be interchanged in the First and Second Terms of successive summers. These courses will be given by members of the Physical Sciences staff in coöperation with the Board of Examinations and the Department of Education:

Physical Sciences 294. An Integrated Course in the Physical Sciences for Teachers of High School and Junior Colleges.—The content of this course is essentially the same as in the one-year Physical Science General Course in the College, but the level of mastery required is higher than in the latter. Opportunity is given for participation in presenting lectures and in conducting discussion sections. The First Term includes the following topics: molecular and atomic nature of matter, the chemical reaction, oxidation and reduction, atomic structure and chemical behavior, carbon compounds, geologic processes, weather and climate, and history of the earth. The Second Term covers mathematics as a tool, mathematics as a science, matter and energy, heat, electricity, radiant energy, the solar system, the sidereal universe. 2 C's. (or 1 C. either Term). 9:00–11:00, Stephenson and Staff.

Physical Sciences 295. Problems in the Teaching of Integrated Physical Science Courses in High School and Junior College.—Open to those students only who are enrolled in *Physical Sciences 294.* Problems relating to the determination of objectives, organization of materials, methods of presentation, and the methods and technics of examination will be discussed. C. (or $\frac{1}{2}$ C. either Term). 11:00, Ashford and Staff.

SUMMER CHANGE OF ADDRESS

BETWEEN the dates of June 15 and September 5, all correspondence for the JOURNAL should be addressed to: JOURNAL OF CHEMICAL EDUCATION, WOODS HOLE, MASSACHUSETTS.

Liquid Ammonia Research in 1940—A Review[1]

GEORGE W. WATT and WILLIAM B. LESLIE

The University of Texas, Austin, Texas

WHILE earlier reviews in this series appear to have been reasonably comprehensive, no such claim can be made for the present paper. This situation is due entirely to irregularities in the distribution of foreign periodicals. The writers are informed that some scientific periodicals in Europe have suspended publication while others no longer attempt distribution. Work which has been described in literature unavailable at this writing will be included in future reviews as the necessary information becomes available.

I. PHYSICO-CHEMICAL STUDIES

The absorption spectra of liquid and solid ammonia in the ultra-violet (5000–2000 A.) region at temperatures near the melting point have been photographed using layers of 1–28 mm. thickness (*8*). The banded spectrum of gaseous ammonia becomes continuous in the liquid and solid states. The spectra of the three states are characterized by large displacements toward the ultra-violet with change in state from gas to liquid to solid. These changes in spectra are attributed to alterations in molecular symmetry resulting from increasing association. Similar displacements have been observed in the spectra of gaseous, liquid, and solid water which is isoelectronic with ammonia and is highly associated. In the infra-red (*9*) region (10,140–5000 A.), the spectra of the solid and liquid were found to be essentially identical and considerably richer than that of gaseous ammonia. Relative to the spectrum of the gas, the absorption bands of the liquid are displaced toward the red and there is a comparable displacement with change in state from liquid to solid. As in the case of the ultra-violet region, these differences appear to be due to structural deformations resulting from association. Apparatus and experimental technics for the study of the absorption spectra of solutions in liquefied gases over the temperature range of −70° to 70°C. have been described by Shatenshtein and Israilevich (*10*). They have investigated the spectra of solutions of a number of aromatic nitro and azo compounds in liquid ammonia and in liquid ammonia solutions of potassium amide. The acid-base equilibria in these solutions were shown to be dependent upon the properties of the solvent and upon the presence of proton acid or non-proton acid-like substances. In reaction with a base such as potassium amide, aminoazo compounds behave as proton acids, while dimethylaminoazo and azoxy compounds react as non-proton acid-like substances. Shatenshtein (*11*) has published detailed descriptions of apparatus suitable for the study of physico-chemical properties of solutions in liquefied gases under pressure, and for the study of reactions in such solvents. It is pointed out that a variety of types of apparatus may be had by the proper assembling of certain glass and metal units. Among others, there are described methods and equipment for use in the measurement of viscosity, surface tension, density, conductivity, solubility of solids and liquids, as well as apparatus adaptable to titration and extraction processes.

The results of a comparative study of the apparent molar volumes of ammonium chloride, bromide, and nitrate, and sodium chloride, nitrate, and nitrite, in ammonia and in water have been described by Akhumov (*12*). In general, it was found that the values for the apparent molar volumes of these salts in ammonia are smaller than those for aqueous solutions of the same concentration and that the increase in apparent molar volume with increase in concentration is greater for ammonia than for water solutions. Values for the specific gravities of solutions of sodium in liquid ammonia over the temperature range −30° to 30°C. and corresponding to concentrations from zero to saturation have been published (*13*). Values for the apparent molal volume and partial molal volume of sodium in liquid ammonia have been calculated.

The difference in vapor pressure between ordinary liquid ammonia and a sample of the liquid containing 70.6 per cent $N^{15}H_3$ has been measured (*14*), and the difference in heats of vaporization, boiling points, and melting points has been computed.

A detailed study of the liquid–vapor equilibria in the system ammonia–methane–nitrogen has been made by Bolshakov and Lebedeva (*15*). The experimental methods, which are described in detail, involve the use of an electromagnetic mixer placed inside the autoclave. Among other results which are too extensive for inclusion here, the solubility of pure methane in liquid ammonia at pressures from 50 to 600 atmospheres over a temperature range of −20° to 50°C. has been calculated from experimental data. The solubilities of sodium, potassium, and ammonium carbonates and sulfates in ammonia-water mixtures have been determined at concentrations from zero to one hundred per cent ammonia and at temperatures from 20° to −30°C. (*16*). The solubilities of these salts approach zero at an ammonia concentration of one hundred per cent. A study of the 20° isotherm for the system liquid ammonia–ethyl alcohol gave no indication of the formation of compounds of the two constituents (*17*).

Apparatus and methods useful in studying electrocapillary curves for liquid ammonia solutions at or near room temperature have been described (*18*). Curves for mercury in liquid ammonia solutions of 1 *N* NH_4NO_3, 1 *N* NH_4NO_3 and 0.5 *N* NaCl, 1 *N* NH_4NO_3 and 0.5 *N*

[1] For earlier papers in this series see references (*1–7*).

NaBr, and 1 N NH_4NO_3 and 1 N KI were obtained at 0°C. The calculated capacity of the electric double layer on mercury was found to be 11 μf./cm.^{2}. In aqueous solutions, halide ions are adsorbed at the mercury–solution interface and cause a shift of the maximum of the electrocapillary curve. A similar behavior was observed in the case of the liquid ammonia solutions investigated. Measurement of the decomposition potentials of certain salts in liquid ammonia and in water solutions (*19*) has shown that the values for ammonium salts are lower for ammonia solutions than for the corresponding aqueous solutions. The opposite relationship, however, was found for salts containing an alkali metal cation. The values reported are reproduced in Table 1.

TABLE 1

	NH_4Cl	*NH_4Br*	*NH_4NO_3*	*KBr*	*KI*	*$NaNO_3$*
NH_3	1.07	0.92	1.32	2.43	2.87	2.52
H_2O	1.76	1.46	2.04	1.74	1.16	2.15

The potential of the cell,

$$Cu^+ \left| \begin{array}{c} CuI \\ 0.1\ N \end{array} \right| \begin{array}{c} KNO_3 \\ Satd. \end{array} \left| \begin{array}{c} Pb(NO_3)_2 \\ 0.1\ N \end{array} \right| Pb^-$$

in liquid ammonia at −50° has been found to be 0.0524 e. v. (*20*). With respect to $E_{Rb} = 0$, the potential of the Cu/Cu^+ electrode is 2.34 as compared with the value (from earlier investigations) of 2.36 for the Cu/Cu^{++} electrode.

Glikman (*21*) has found that concentrated solutions of sodium in liquid ammonia exhibit both metallic and electrolytic conduction, a behavior previously demonstrated by Kraus (*22*). Using carefully purified materials and an apparatus which has been described in detail, Häsing (*23*) has studied the photoelectric properties of both concentrated and dilute solutions of sodium in liquid ammonia. A threshold value of 773–970 mμ and work function of 1.60–1.40 e. v. are reported. Study of concentrated solutions provided evidence for a surface effect which is attributed to the presence of free electrons, while dilute solutions exhibited volume effects believed due to loosely associated electrons. The introduction of Häsing's paper includes a concise review of accumulated evidence bearing on the nature of solutions of metals in liquid ammonia.

II. INORGANIC REACTIONS

Diborane diphosphine, $B_2H_6 \cdot 2PH_3$ (or $BH_3 \cdot PH_3$), has been found to be difficultly soluble in and unreactive toward liquid ammonia at −75° (*24*). At higher temperatures, however, the boron compound dissolves readily and reacts with ammonia to form a white pasty solid which is more stable than diborane diphosphine and which is believed to be diborane phosphine ammine, $B_2H_6 \cdot PH_3 \cdot NH_3$. During the formation of this substance, the rate of evolution of phosphine increases with increase in temperature and reaches a maximum at 0°. Pyrolysis (200°) of $B_2H_6 \cdot PH_3 \cdot NH_3$ yielded some of the volatile cyclic $B_3N_3H_6$ (the so-called "inorganic benzene") but gave no evidence of the formation of a phosphorus analog having similar properties. It has been shown (*25*) that $B_3N_3H_6$ reacts with liquid ammonia at room temperature to form a white amorphous solid which darkens upon exposure to air. The quantity of ammonia taken up depends upon the time of reaction. The structure proposed by Schlesinger and Burg (*26*) for the product obtained by the action of liquid ammonia on diborane has been criticized by Agronomov (*27*). An alternative explanation based on the assumption that the product should be formulated as the ammine, $BH_3 \cdot NH_3$, has been offered. Aluminum borohydride, AlB_3H_{12} (prepared by the reaction between trimethylaluminum and diborane), has been shown to react with liquid ammonia at −80° to form a mixture of clear crystals and amorphous white solid (*28*). On warming to 0°, only the amorphous material remained. When the reaction mixture was warmed to 25° and allowed to stand for twenty hours, the insoluble product consisted wholly of the crystalline material. As a result of the study of the vapor pressures of the system, $(CH_3BO)_3$–NH_3, Burg (*29*) has shown that methylboric anhydride forms a fairly stable monammonate, $(CH_3BO)_3 \cdot NH_3$, and a less stable diammonate, $(CH_3BO)_3 \cdot 2NH_3$. This study provided no evidence of the existence of higher ammonates.

Fowler and Kraus (*30*) have reported that reaction occurs between liquid ammonia solutions of aminotriphenylboron and each of the following salts: sodium benzhydrolate, sodium (or potassium) triphenylcarbinolate, and sodium phenylacetate. Less extensive reaction was observed using sodium phenolate. The identity of the products of these reactions was not established nor were the chemical and physical properties of the reaction products investigated extensively.

The behavior of a number of covalently saturated ammines of chromium, cobalt, and nickel toward liquid ammonia (−76.5° to 19°) has been investigated by Spacu and Voichescu (*31*). All of the ammines studied were found to combine with additional molecules of ammonia. For example, $Cr(NH_3)_6Cl_3$ at low temperatures appeared to form ammonates containing seven, eight, and fourteen molecules of ammonia in addition to the six molecules in the original complex, but with increase in temperature the added molecules of the solvent were lost and the original ammine was recovered at room temperature. To illustrate another type of behavior observed, *trans*-$(Coen_2Cl_2)Cl$ was found to add up to four molecules of ammonia at −76.5°, while, when treated with liquid ammonia over longer periods of time at higher temperatures, there were formed mixtures of ammonates as well as products in which chlorine in the complex was replaced by ammonia. Only in these latter cases were there produced any changes in color. As a general conclusion, it is suggested that in the majority of cases the ammonia molecules added in the formation of the unstable higher ammonates occupy positions in a sphere of bonding other than that containing the ammonia molecules in the original complex. The preparation of $Cr(NH_3)_6Br_3$ has been reported by Hein and Kraft (*32*). Anhydrous

chromic chloride was treated with liquid ammonia at −50° and the resulting hexammine was converted (in aqueous solution) to the nitrate, which in turn was converted to the corresponding bromide. A number of ammonates of WO_2Cl_2 and WCl_6 have been reported (*33*) as resulting from the action of liquid ammonia at low temperatures. The compositions of these ammonates together with the temperatures at which their formation was observed are:

$WO_2Cl_2 \cdot 12NH_3$ (−75°); $\cdot 10NH_3$ (−66°); $\cdot 5NH_3$ (−34°); $\cdot 4NH_3$ (34·8°); $\cdot 3NH_3$ (100°)

$WCl_6 \cdot 16NH_3$ (−75°); $\cdot 14NH_3$ (−52°); $\cdot 8NH_3$ (−30°); $\cdot 6NH_3$ (0°)

At temperatures above 0°, tungsten hexachloride is ammonolyzed. VanValkenburgh and Schoffman (*34*) have made a number of unsuccessful attempts to prepare an ammine of vanadium tetrachloride. A vigorous reaction was observed to occur between the tetrachloride and liquid ammonia, but the anticipated ammine was not found. It is rather apparent that these workers have overlooked completely, among other things, the possibility of ammonolysis of the halide.

The very slow reaction between potassium nitrate and potassium amide in liquid ammonia at room temperature has been shown to occur in accordance with the equation (*35*)

$$3KNO_3 + 3KNH_2 \longrightarrow 3KNO_2 + N_2 + 3KOH + NH_3$$

This reaction is catalyzed by Fe_2O_3, Co_2O_3, NiO, and CuO. Less active catalysts employed include Mn_3O_4, Al_2O_3, ZnO, and Cr_2O_3. There was no evidence of appreciable formation of azide in reactions effected at room temperature. The reaction between potassium nitrite and potassium amide,

$$KNO_2 + KNH_2 \longrightarrow 2KOH + N_2$$

was found to be extremely slow at room temperature and to be catalyzed by Fe_2O_3 and Co_2O_3.

Finely divided and highly reactive calcium required by Johnson and co-workers (*36*) in the study of the formation of calcium hydride was obtained by dissolving calcium in liquid ammonia at −80°, removing the greater part of the solvent *in vacuo* at −80°, and the remainder at room temperature. Amide formation was suppressed by using pure calcium, by operating at low temperatures, and by reducing the time of contact to a minimum.

Diphenylthallium bromide has been found to yield triphenylthallium and thallium metal, on treatment with one equivalent of sodium in liquid ammonia (*37*). The use of liquid ammonia for the extraction of sodium and potassium nitrates from nitrate deposits has been discussed by Vasil'ev (*38*).

III. ORGANIC REACTIONS

1. Ammonolysis

It has been reported that 1-chloro-*n*-dodecane when heated at 110°C. with liquid ammonia diluted with ethyl alcohol reacts to form a mixture of laurylamine and dilaurylamine (*39*). The reactions of some other 1-chloro-paraffins with liquid ammonia-alcohol mixtures at temperatures above the critical temperature of liquid ammonia were also studied. Cetyl bromide and octadecyl chloride react with liquid ammonia at 50° to form the corresponding primary amines in 40 and 35 per cent yields, respectively (*40*). Docosyl bromide fails to react with ammonia under similar conditions. The possible formation of piperazine in nearly quantitative yield by the reaction between ethylene dibromide and anhydrous ammonia has been suggested (*41*).

In an effort to prepare cyameluric triamide, Redemann and Lucas (*42*) have treated cyameluryl chloride, $C_6H_7Cl_3$, with anhydrous liquid ammonia over a period of twenty hours at room temperature. After removal of the excess ammonia and of the ammonium chloride formed in the reaction, there remained a flocculent solid containing 60.18 per cent nitrogen. The calculated nitrogen content of the triamide sought is 64.2 per cent.

The action of liquid ammonia at room temperature on 3,3-di(bromomethyl)oxacyclobutane has been shown to result in the formation of 3,3-di(aminomethyl)-oxacyclobutane dihydrobromide (*43*).

In the course of the preparation of ethyl cyclopropyl ketimmonium chloride, $\underbrace{CH_2CH_2}CHC(=NH_2Cl)C_2H_5$, the compound formed between ethyl magnesium bromide and cyclopropyl cyanide was decomposed by adding an ethereal solution of the addition compound to an excess of liquid ammonia at its boiling point (*44*). The ketimine thereby liberated,

$$\underbrace{CH_2CH_2}CHC(C_2H_5)=NMgBr + NH_3 \rightarrow \underbrace{CH_2CH_2}CHC(C_2H_5)=NH + MgNH_2Br$$

was subsequently converted to the hydrochloride. Ruff and Willenberg (*45*) have reported that hexafluoroazomethane reacts with liquid ammonia to form products which could not be separated and identified. The reaction between liquid ammonia and bis(trifluoromethyl)amine has also been observed but ammonium fluoride was the only product identified.

Cannabidiol (a compound present in the red oil extracted from Minnesota hemp, *Cannabis sativa*) has been isolated by ammonolyzing cannabidiol *bis*-3,5-dinitrobenzoate by means of a mixture of toluene and liquid ammonia over a period of five hours at room temperature (*46*). The solid 3,5-dinitrobenzamide was removed and the cannabidiol purified by distillation under reduced pressure. Cannabidiol from Egyptian hashish has been isolated by this same procedure (*47*).

Although ketene diethylacetal and water react vigorously, the acetal has been found to be unreactive toward ammonia at 25° (*48*). However, reaction at 100° appears to be complete in three hours and the products of this reaction are ethyl alcohol, acetonitrile, acetamidine, and ethyl orthoacetate. The reactions

indicated by the following equations account for the observed products:

$$CH_2=C(OC_2H_5)_2 + NH_3 \longrightarrow [CH_3C(OC_2H_5)_2NH_2] \longrightarrow C_2H_5OH + CH_3C(OC_2H_5)=NH$$

$$CH_3C(OC_2H_5)=NH + NH_3 \longrightarrow \text{(}-C_2H_5OH\text{)}$$

$$C_2H_5OH + CH_3C(NH_2)=NH \xrightarrow{-NH_3} CH_3CN$$

$$CH_2=C(OC_2H_5)_2 + C_2H_5OH \longrightarrow CH_3C(OC_2H_5)_3$$

The preparation of mandelamide in 62 per cent yield by a method based on the work of Oeda (*49*) has been described by Audrieth and Sveda (*50*). The method involves the condensation of mandelic acid with acetone followed by ammonolysis of the condensation product by liquid ammonia at its boiling point.

It has been shown that 4-bromoisoquinoline is ammonolyzed to the corresponding 4-amino compound (17 per cent yield) by heating with liquid ammonia in the presence of copper and copper salts for seven hours at 106° (*51*). To obtain a comparable yield (16 per cent) using aqueous ammonia required heating for sixteen hours at 250°. However, the bromide with potassium or sodium amide in liquid ammonia yielded only a tar. Isoquinoline-4-carboxylic acid was found to react with potassium amide in liquid ammonia to give a slightly soluble potassium salt, which passed into solution with the evolution of hydrogen to form the potassium salt of 1-amino-isoquinoline-4-carboxylic acid.

2. *Reactions of Alkali Amides*

The interaction of equimolecular quantities of β-methyl-allyl chloride and sodium amide in liquid ammonia at its boiling point has been shown to result in the formation of 2,5-dimethylhexatriene in 27 per cent yield (*52*). Use of less than one equivalent of sodium amide led to the isolation of the intermediate chloro-2,5-dimethylhexadiene which was converted to 2,5-dimethylhexatriene. Similarly, treatment of two mols of allyl chloride with one mol of sodium amide yielded the anticipated chlorohexadiene.

Ethyl butylidene malonate has been shown to form a sodium salt upon treatment with a solution of sodium amide in liquid ammonia (*53*);

$$CH_3CH_2CH_2CH=C(CO_2C_2H_5)_2 + NaNH_2 \longrightarrow [CH_3CH_2CH^+ CHC(CO_2C_2H_5)_2]^-Na^+ + NH_3$$

By similar reactions the sodium enolates of ethyl isopropylidene malonate, ethyl cyclopentylidene malonate, and ethyl 1-methyl-propylidene malonate have been prepared (*54*). Acidification of these salts yielded the corresponding βγ unsaturated malonic esters.

An unsuccessful attempt to dehydrate phenylbenzylcarbinol by means of sodium amide in liquid ammonia has been reported (*55*). The carbinol and sodium amide in a mixture of liquid ammonia and ether were allowed to stand for one week in a sealed tube at room temperature. Ninety per cent of the carbinol was recovered.

3. *Reactions of Solutions of Metals*

A study of the reduction of benzotriazoles by sodium in liquid ammonia (*56*) makes evident the fact that more extensive reduction may be effected by nascent hydrogen than by the electron. 1,2,3-Benzotriazole reacts with sodium in liquid ammonia at its boiling point without liberation of hydrogen to form equimolecular quantities of the sodium salt and what is believed to be a dihydro derivative. Nascent hydrogen, generated by the addition of ammonium bromide to a solution of sodium, reduces the sodium benzotriazolate to *o*-phenylenediamine. However, hydrogen generated by the interaction of potassium and liquid ammonia in the presence of iron, does not reduce the potassium salt of 1,2,3-benzotriazole. Active hydrogen reduces 2-methyl-1,2,3-benzotriazole to *N*-methyl-*o*-phenylenediamine. Since reduction may result from the action of hydrogen as well as the electron, it appears that upon completion of a reduction employing sodium in liquid ammonia, any excess sodium should be destroyed without the generation of hydrogen. The use of sodium nitrate or mercury has been suggested for this purpose.

Doeuvre (*57*) has again indicated that citronellol cannot be separated quantitatively from geraniol using sodium in liquid ammonia. This procedure, formerly proposed by Chablay, involves the elimination of the geraniol by reduction, the citronellol remaining unchanged.

Employing the method of du Vigneaud (*58*), Harington and Moggridge (*59*) have utilized the reducing action of sodium in liquid ammonia in the removal of the toluene-sulfonyl residue from *N*-*p*-toluenesulfonyl glutamic acid amide. An aqueous solution of the crude product on treatment with benzyl chloroformate gave a good yield of *N*-carbobenzyloxyisoglutamine. In connection with the preparation of derivatives of certain carcinogenic hydrocarbons, Wood and Fieser (*60*) have prepared 1,2-benzanthryl-methyl-S-*l*-cysteine. 10-Chloromethyl-1,2-benzanthracene was added to an ammonia solution of sodium cysteinate, obtained by reducing *l*-cystine with sodium in liquid ammonia. The synthesis of diglycyl-*l*-cystine has been described by Greenstein (*61*). Carbobenzoxyglycine was converted to the acid chloride which was then treated with *l*-cystine to form dicarbobenzoxyglycyl-*l*-cystine. This product, upon reduction by means of a solution of sodium in liquid ammonia at its boiling point, yielded the crystalline peptide.

In the course of the study of the oxidation of cholesterol, Köster and Logemann (*62*) have prepared 1,7-dihydroxy-2,13-dimethyl-1-ethynyl-$\Delta^{9,14}$-dodecahydrophenanthrene by the addition of oxo-dimethyl-dodecahydrophenanthrol-acetate to a solution of potassium acetylide in liquid ammonia below its boiling temperature. The mixture was allowed to stand overnight and then decomposed with water.

Freudenberg and co-workers (*63*) have reported unsuccessful attempts to synthesize a disaccharide by the reactions between alkali metal salts of diacetoneglucose and acetohaloglucoses or diacetone-1-chloromannose. The alkali salts were formed by adding sodium or potassium to liquid ammonia solutions of diacetoneglucose. The corresponding thallium salt was prepared by adding an excess of thallous nitrate in liquid ammonia to an ammonia solution of sodium diacetoneglucose. It is of interest to note that similar disaccharide syntheses have been attempted previously (*64, 65*).

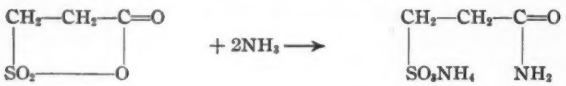
Unsuccessful attempts to methylate ovomucoid (from commercial egg albumen) by the use of methyl iodide in liquid ammonia have been reported (*66*). Like results attended efforts to methylate the carbohydrate residue obtained from ovomucoid. Freudenberg and Boppel (*67*) have shown that the maximum possible methylation of potato starch (45.6 per cent OCH_3) is accomplished using sodium and methyl iodide in liquid ammonia. All attempts at further methylation were unsuccessful. Freudenberg and Plankenhorn (*68*) have prepared hexamethylmaltose anhydride by treating maltose anhydride with a liquid ammonia solution of potassium, removing the solvent ammonia, and adding diethyl ether and an excess of methyl iodide. Employing a procedure previously described (*69*), Hess and co-workers (*70*) have extended their study of the methylation of starch.

Kharasch and co-workers (*71*) in a continuation of their work on the action of sodium in liquid ammonia on esters have found new evidence in support of the reaction mechanism formerly proposed (*72*). The action of one equivalent of sodium yields a free radical, while two equivalents produce a very reactive organosodium compound. It has been reported that *p*-benzohydryltetraphenylmethane, $(C_6H_5)_2CHC_6H_4C(C_6H_5)_3$, is stable in the presence of sodium in liquid ammonia (*73*).

The work of Gilman and Bailie (*74*) on organometallic compounds of lead has been described by Bailie (*75*). It has been reported (*76*) that sodium in liquid ammonia reacts with a mixture of $[(CH_3)_3Sn]_3OI$ and water to yield sodium trimethyl stannide and a small amount of an unidentified hydrocarbon gas. The action of sodium on $[(CH_3)_3SnOH]_2Sn(CH_3)_3I$ in liquid ammonia also yields a hydrocarbon gas, and no hydrogen. A similar reaction had been carried out by Kraus and Bullard (*77*), except that the bromide was used instead of the iodide, and hydrogen was evolved rather than a hydrocarbon gas. A comprehensive review on the molecular compounds of alkytin halides has been presented by Harada (*78*).

4. Other Organic Reactions

The addition of β-sulfopropionic anhydride to a large excess of liquid ammonia has been reported to yield the ammonium salt of β-sulfopropionamide (*79*).



The preparation of *d*-arabonamide by the action of liquid ammonia on *d*-arabonic lactone has been reported (*80*).

o-Cyanobiphenyl has been reduced to *o*-phenylbenzylamine by catalytic hydrogenation (Raney nickel) at 120° in a solvent medium consisting of a mixture of ether and liquid ammonia (*81*).

Further studies on the dietary effects produced by the ammonolysis of casein, starch, yeast, etc., have been described by Roberts and Horvitz (*82*). In connection with the work of these authors, it should be pointed out that in an earlier paper in this series (*83*) it was erroneously stated that certain conjugation products of epinephrine produce a *greater* rise in blood pressure in dogs than does epinephrine. As is clearly shown by the work of Roberts and Horvitz, however, it should have been indicated that the pressor action is not greater but rather is more prolonged. The usefulness of liquid ammonia as a medium for the study of compounds of biochemical significance has been pointed out by Roberts (*84*).

IV. PATENTS

Processes relating to methods of preparation of a number of inorganic substances have been patented. Ammonium fluoride (*85*) has been produced by neutralizing concentrated hydrofluoric acid with liquid ammonia, followed by evaporation of the solvent under such conditions as to obviate the formation of an acid salt. Hydrated salts of iron, cobalt, and nickel are claimed as catalysts for the conversion of an alkali metal to the corresponding amide (*86*) in a process so conducted that liquid ammonia is present in excess throughout the formation of the amide. There continue to appear in the literature patents concerned with the production of ammonium carbamate (*87*) by treatment of anhydrous liquid ammonia with liquid or solid carbon dioxide. By interaction of alkali nitrates and ammonium carbamate in liquid ammonia, alkali carbamates have been formed and subsequently converted to alkali carbonates (*88*). Sulfur nitride (*89*) has been formed by the reaction between sulfur monochloride and an excess of anhydrous liquid ammonia or liquid ammonia containing a non-aqueous diluent such as toluene. By interaction of an alkali metal and an alkali sulfamate in liquid ammonia, there have been produced *N*-substituted sulfamates (*90*). Thus, $NaNHSO_3Na$ may be produced and subsequently converted to the desired substituted sulfamates by reaction with organic halides, halogens, etc. Methods for the dehydration (*91, 92*) and removal of soluble impurities such as chloride and chlorate (*93*) from caustic alkalies involve extraction with liquid ammonia. The dispersion of aluminum, sulfur, a sugar, nitro compounds, etc., in chlorate or perchlorate explosives (*94*) has been accomplished by dissolving or suspending the ingredients in anhydrous liquid ammonia followed by crystallization.

A number of recent patents relate to the formation of alkali acetylides (*95*) by the reaction between an alkali metal and acetylene in liquid ammonia and the utilization of these products in the preparation of a wide variety of organic substances. Acetylides prepared in this manner have been used in the production of acetylenic acids by reaction with carbon dioxide in the presence of inert hydrocarbon diluents either in the presence (*96*) or absence (*97*) of liquid ammonia. Treatment of polyhydrocyclopentanophenanthrene compounds containing one or more keto groups with solutions of potassium acetylide in liquid ammonia has been patented as a means of producing acetylenic derivatives (*98*). For example, dehydroandrosterone may by this method be converted to $\Delta^{5,6}$-17-ethynyl-androstene-3,17-diol. Another process is concerned with the production of ethynyl carbinols (*99*) by treatment of ketones with sodium acetylide in liquid ammonia. Thus 1,1-ditridecyl-2-propyn-1-ol may be produced from myristone and sodium acetylide. Similarly, examples are given of the use of sodium vinyl acetylide or sodium carbide. In reaction with dialkyl sulfates or alkyl halides in liquid ammonia, sodium carbide has been used in the preparation of dialkylacetylenes (*100*). Reactions involving metal acetylides and organic nitrogen compounds have been used as a means of preparing amino compounds containing acetylenic linkages (*101*). A recent patent concerned primarily with operative details relates to the production of urea from ammonia and carbon dioxide (*102*). Unconverted ammonia and carbon dioxide are recovered in the form of a slurry of ammonium carbamate in liquid ammonia and thereafter recycled into the autoclave in which urea is formed.

Patents involving the use of liquid ammonia as a reaction medium in the production of melamine (2,4,6-triamino-1,3,5-triazine) have been referred to in an earlier review (*103*). Recent patents (*104, 105, 106*) are concerned with improvements in procedure designed to provide a product of greater purity in more satisfactory yields. Another patent has been issued covering a process for the preparation of acid amides (*107*) by the ammonolysis of naturally occurring esters of aliphatic monocarboxylic acids by liquid ammonia under pressure and at temperatures of 100° to 130°C. The production of oleic amide from olive oil is cited as an example. High yields and short time of reaction are claimed as advantages in a process for the preparation of reaction products of ammonia and aldose sugars (*108*). The sugar is heated with an excess of anhydrous liquid ammonia and an acid catalyst for two or three hours at 50°–90°C. That such products may be obtained by the interaction of sugars and liquid ammonia was demonstrated by Muskat (*109*) in 1934.

Other processes utilizing liquid ammonia involve the formation of alkali metal salts of cellulose (*110*) and the use of these salts as intermediates in the production of cellulose ethers (*111*) and xanthates (*112*). Anhydrous liquid ammonia has also been used in the purification of cellulose triacetate (*113*) and in the stabilization of derivatives of starch and cellulose (*114, 115*).

The formation of 1,4-dihydrobenzene and dihydrotoluene (*116*) from benzene and toluene, respectively, has been accomplished by the reduction of the aromatic hydrocarbons by means of an alkali or alkaline earth metal in liquid ammonia in the presence of a hydrolytic agent, such as methyl alcohol, which reacts with the evolution of hydrogen.

V. GENERAL

A comprehensive and critical review of the literature on ammonolytic reactions has been presented by Fernelius and Bowman (*117*). There are included studies on the ammonolysis of a wide variety of inorganic, organic, and organo-metallic compounds, together with nearly three hundred primary references. This valuable review paper should be consulted by anyone interested in and contemplating work with the type of reaction concerned. Audrieth and co-workers (*118*) have provided a thorough discussion of the chemistry of a group of compounds which, in the sense of Franklin's nitrogen system of compounds, may be considered as mixed aquo-ammonosulfuric acids or derivatives thereof. Substances covered in this review include: sulfamic acid, $HOSO_2NH_2$; sulfamide, $SO_2(NH_2)_2$; imidodisulfonic acid, $HN(SO_2OH)_2$; nitrilosulfonic acid, $N(SO_2OH_3)$; imidodisulfamide, $HN(SO_2NH_2)_2$; sulfimide, $HNSO_2$; and the cyclic trisulfimide, $(HNSO_2)_3$. Numerous primary references are cited. A brief discussion of types of reaction which may be effected in liquid ammonia and reagents available for reactions in this solvent has been given by Kraus (*119*). Other papers of general interest include a discussion of the utilization of liquid ammonia as a motor fuel (*120*), and a historical paper in which the question of priority in the liquefaction of ammonia (*121*) is raised.

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Isotopes in the Study of Plant Growth[1]

A. KEITH BREWER

Bureau of Plant Industry, U. S. Department of Agriculture, Washington, D. C.

THE development of the isotope technic during the past few years has placed an entirely new means of investigation at the disposal of the biologist. It is now possible, by using isotopes as tracers, to follow the course of an element through complicated biological processes. The method has been perfected to the point where it greatly facilitates the study of many problems which have long been under investigation; in addition it bids fair to open new fields of research not amenable to conventional methods.

Isotopes can be classified as natural and artificial; both exist in a stable or radioactive form.[2] At present biological investigations are confined to the use of natural stable isotopes and to artificial radioactive isotopes. A comprehensive study of all elements necessitates using both types of isotopes. Several of the elements, including phosphorus, sodium, and fluorine, do not have natural isotopes; therefore the artificial must be used. Again, for several of the light elements, the artificial radioactive isotopes are of such a short life that their use as tracers is impossible. Fortunately suitable isotopes of all elements of interest appear to be obtainable.

STABLE ISOTOPES

The utilization of isotopes involves two steps: first, their preparation and second, their analysis. The problem is complicated by the fact that these steps are entirely different for stable and for radioactive isotopes. Biological investigations with stable isotopes have so far been limited to heavy hydrogen, carbon, and nitrogen. The method most largely used for concentrating these isotopes is due to Urey.[3] Slight differences in the chemical activities of the isotopes are utilized to induce small increments at lower concentrations which are then enhanced many-fold by refluxing. Commercial production of N^{15} and C^{13} by such a method is now being undertaken. Various other methods for isotope separation have also been developed.[4,5] It now seems certain that within a few years methods will be perfected for the concentration of most of the natural isotopes.

Analysis of stable isotopes requires a mass spectrograph. In this apparatus atoms are separated in a magnetic field due to differences in their momenta. Several simple designs have been described recently.[6]

A characteristic isotope analysis is illustrated by the mass spectrogram for lithium shown in Figure 1. In this figure the isotope current received by the collector is plotted against the magnetic field strength; this is calibrated in terms of mass number. It will be observed that lithium has two natural isotopes, Li^6 and Li^7 in ratio $Li^7/Li^6 = 11.6$.[7] Similar spectrograms for

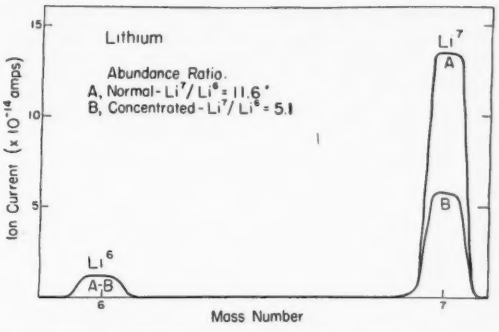

FIGURE 1.—MASS SPECTROGRAM FOR NORMAL AND CONCENTRATED LITHIUM

nitrogen give the ratio $N^{14}/N^{15} = 130$ and for carbon $C^{12}/C^{13} = 101$.

The quantity of material required for an analysis is of particular concern to the biologist. In the case of potassium or lithium an amount of tissue ash containing about 10^{-8} grams of the element is all that is needed, since no chemical manipulation is involved; while for nitrogen and carbon dioxide about 0.1 cc. of gas is necessary.

The method of using stable isotopes as tracers can be seen by referring to the mass spectrogram for lithium. When the enriched lithium, in which the isotope ratio has been changed to $Li^7/Li^6 = 5.1$, is added to a plant culture solution, any deviation from 11.60 in the isotope ratio of the plant indicates the presence of tracer atoms. Divergence of the isotope ratio between 11.5 and 5.1 indicates the relative ratio of initial lithium to isotopic lithium in the tissues.

RADIOACTIVE ISOTOPES

Preparation and analysis of artificial radioactive isotopes require entirely different technics from those described for natural isotopes. Radioactive isotopes

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are produced most successfully by adding a neutron to the nucleus. For instance, when phosphorus is bombarded by several million volt deuterons, the following reaction takes place:

$$_{15}P^{31} + {}_1D^2 \rightarrow {}_{15}P^{32} + {}_1H^1$$

The P^{32} so synthesized, while possessing the chemistry of P^{31}, is unstable and decomposes, emitting a beta ray according to the equation

$$_{15}P^{32} \rightarrow {}_{16}S^{32} + \beta$$

Since $_{16}S^{32}$ is the most abundant stable isotope of sulfur, it represents the end-product of the reaction. Reaction takes place spontaneously, going to half completion in 14.4 days.

Radio isotopes are best detected by a beta-ray Geiger counter. A model capable of detecting faint beta rays, particularly suitable for plant investigations, has been developed in the Bureau of Plant Industry.[8] This counter has a background count of about two per minute instead of the 25 obtained with commercial counters. Its efficiency is nearly 100 per cent for rays over 50,000 volts. The beta-ray window is made of aluminum foil 0.0003 inch thick. In operation each beta ray entering the counter gives rise to an electrical impulse which is amplified to operate a counting mechanism.

STUDIES WITH STABLE AND RADIOACTIVE ISOTOPES

The detection of stable and radioactive isotopes within the plant requires different technics. For stable isotopes it is necessary to excise a section of the plant, reduce the nitrogen to elemental nitrogen, oxidize the carbon to carbon dioxide, or ash the material for potassium, in order that the isotope ratio can be determined by the mass spectrograph. On the other hand, for radioactive isotopes, it is only necessary to bring the

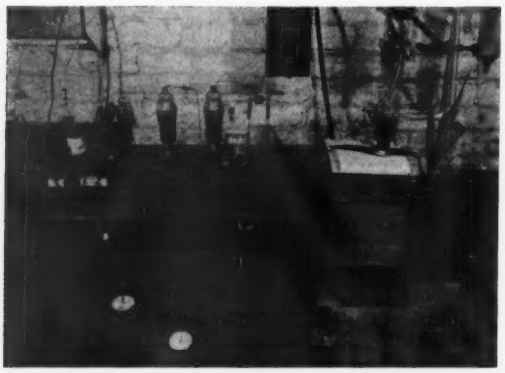

FIGURE 2.—COUNTER AND ASSEMBLY FOR MEASURING BETA RAY EMISSIVITY PER SQUARE CENTIMETER OF LEAF

unexcised leaf or stem beneath the window of the counter to analyze quantitatively the material taken up by the tissue. A count can be made in one minute. The method is illustrated in Figure 2 where a section of leaf is shown exposed below the counter window. From the number of counts recorded in one minute, the quantity of radioactive sodium and its accompanying stable sodium absorbed in one square centimeter of leaf can be directly computed.

The advantages of radioactive isotopes over stable isotopes are: (1) readings can be made quickly with extreme ease, (2) it is unnecessary to mutilate the plant, and (3) a series of readings can be made on the same specimen. The disadvantage is that the radio isotopes of many of the elements have a short half-life; for carbon it is 12 minutes, for nitrogen 9.9 seconds, and for lithium 0.88 second. Stable isotopes are preferable, therefore, for processes extending over long intervals. However, a comprehensive study of all the elements necessitates the use of both types of isotopes.

Before proceeding to a description of the actual results obtained by the isotope technic, it is necessary to answer a question which inevitably arises; namely, does the organism respond in the same manner to abnormal isotope concentrations, either stable or radioactive, as it does to the normal element? Some years ago the writer began a detailed study of this problem.[6] Potassium was chosen since it is the only vital element that is naturally radioactive. A number of cases were found where measurable deviations in the K^{39}/K^{41} ratio occur. These deviations are found principally in plants having no vascular system, and in animal tissues. The differences are always small, usually less than one part per 10,000 in atomic weight. Such differences, while significant in themselves, do not interfere with the use of isotopes as tracers, except in the case of hydrogen, where 40 per cent heavy water is lethal to a mouse and where 20 per cent heavy water, injected into the brain of a monkey, produces a condition similar to *dementia praecox*. For radioactive isotopes, the conditions are more complicated. Calculations show that the chance of a positive ion being formed by a beta ray passing through the sensitive region of the gene is small. In consequence there is very little likelihood of a nuclear abnormality being induced in the cell except by very intense radioactivity. However, there is a possibility of chemical action being induced in the cytoplasm by positive ion formation.[9] The effect of such reactions is a problem requiring extensive research. According to Hevesy, radioactivity produces little if any immediate change in cell function. Continued exposure for long periods of time, however, does have an effect, resulting in stimulation for small doses and a detrimental action for large doses. The action of radon on shoots of *Phaseolus multiflorus* is illustrated by Hevesy and Paneth.[10]

STUDIES AT THE BUREAU OF PLANT INDUSTRY

There are two types of problems to be investigated by the isotope technic; those which can be attacked by

[8] BREWER AND BRAMLEY, *J. App. Phys.*, **9**, 778 (1938).

[9] BREWER, *Chem. Rev.*, **21**, 213 (1937).

[10] HEVESY AND PANETH, "A manual of radioactivity," translated by LAWSON, 2nd ed., Oxford University Press, H. Milford, London, **1938**, Fig. 51, facing p. 241.

conventional methods but whose solution is simplified by the use of isotopes, and those which are not amenable to present methods. Unfortunately, while numerous investigations have been carried out, by far the greater number have been with animal rather than with plant material. This is particularly true for stable isotopes, where only limited studies have been made on plant problems.

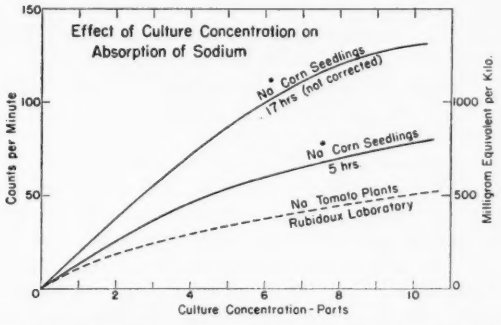
Effect of Culture Concentration on Absorption of Sodium
Na* Corn Seedlings 17 hrs (not corrected)
Na* Corn Seedlings 5 hrs
Na Tomato Plants Rubidoux Laboratory
Counts per Minute
Milligram Equivalent per Kilo.
Culture Concentration - Parts

FIGURE 3.—ABSORPTION OF RADIOSODIUM PER SQUARE CENTIMETER OF LEAF FOR VARIOUS CULTURE CONCENTRATIONS. NOT CORRECTED FOR SODIUM DECAY

To illustrate the applicability of the isotope technic to fertilizer problems, a few of the simple studies on factors influencing the absorption of radiosodium and radiophosphorus, carried out in the Bureau of Plant Industry, will be described. A number of other investigations will be mentioned to show the possibilities of the method.

The absorption of sodium by the leaf of a two-weeks-old corn seedling as a function of the solution concentration, is given in Figure 3. The curves marked 5 hours and 17 hours were obtained from the same set of plants grown in a culture solution containing varying amounts of radiosodium as chloride. The solution of NaCl was diluted to 0.01, 0.02, 0.04, 0.06, and 0.1 *N* by the addition of a sodium-free culture solution. The results are given in counts per minute per square centimeter of leaf. These can be converted to grams by determining the number of counts per unit weight of NaCl. Two plants were tested for each concentration. In making the tests it is simply necessary to expose the same section of the leaf below the counter window and to measure the number of counts during a one-minute interval. The actual time required to adjust the plant and make a reading is about three minutes. Absorption was found not to increase linearly with the culture concentration. No corresponding data by the chemical method are available; however, the results obtained by the Bureau of Plant Industry at its Riverside, California, Rubidoux Laboratory for tomato plants show the same type of decrease in proportionality.

In determining the effect of the root system on the rate of absorption, intact plants were contrasted with plants having their roots cut to one-half inch in length, with plants cut off just above the root system, and with excised leaves. The results show the rate of absorption to be almost identical in all cases.

The rate of absorption of phosphorus and sodium by corn seedlings as a function of time is illustrated in Figure 4. Curves I, II, and III in part 1 show the rate of phosphorus absorption for different culture concentrations. Five minutes after the radiophosphorus was added to the culture media, radioactivity was observed in the leaves six inches from the solution level. Since the plant is uninjured by the measurements, the phosphorus present in various regions of the plant is easily traced. In the average plant the radioactivity reaches final value, depending on the culture concentration, in the course of a few hours in the stem and near the base of the leaves, but in the leaf tips absorption is more gradual; a fairly uniform distribution is finally obtained throughout the plant.

A comparison of curves II and IV is of interest since they were obtained under identical conditions except that plant IV was allowed to stand in a solution containing K_3PO_4 for 24 hours before being placed in the radioactive solution. It appears that the absorption is conditioned by the quantity already present within the plant, as well as by concentration of the culture. Similar results were obtained with excised leaves. Plants which stood for 12 hours in 0.01 *N* K_3PO_4 before they were transferred to a radiophosphorus solution, absorbed in two hours only one-eleventh the quantity of phosphorus taken up by similar plants that had stood an equal period in tap water.

Curve *A*, part 2, shows the rate of absorption of sodium as a function of time.[11] After 14 hours the plant was removed from the culture solution and the roots immersed in tap water. Curve *B* shows the decrease in radioactivity of the roots with time, while curve *C* shows the gain in radioactivity by the tap water. When plants containing radioactive sodium

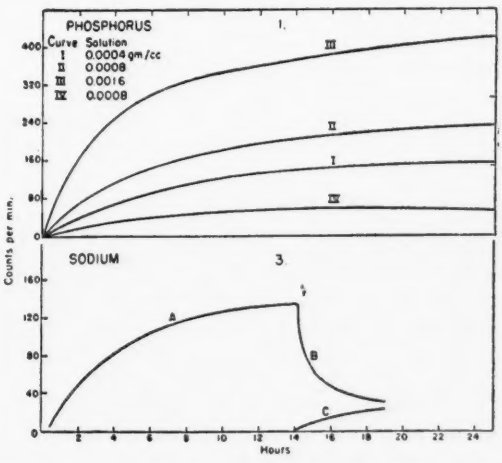

FIGURE 4.—THE ABSORPTION OF RADIOPHOSPHORUS AND RADIOSODIUM BY CORN SEEDLINGS

[11] BREWER AND BRAMLEY, *Science*, **91**, 269 (1940).

were transferred to tap water or to a deficient nutrient medium, the radioactivity in the roots and lower part of the stem decreased rapidly; in the leaves, however, the decrease was very much slower. Phosphorus, under similar conditions, showed no tendency toward elimination from the leaves; the radioactivity decreased slowly but did not disappear completely from the roots.

The effect of culture temperature on sodium absorption is shown in Figure 5. In these tests four corn seedlings were placed in culture solutions at 11°C. and at 33°C. Asbestos boards mounted between the solutions and the leaves made it possible to keep the leaf

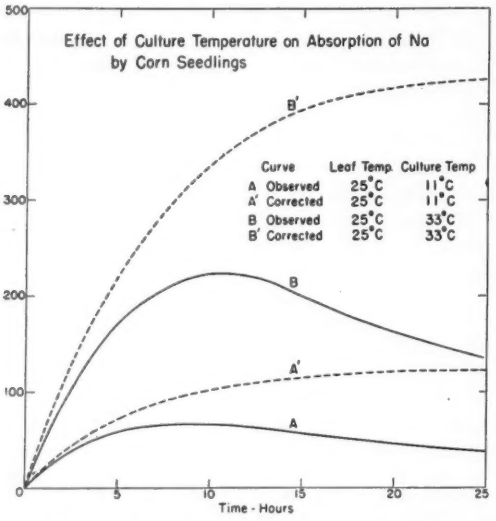

FIGURE 5.—THE ABSORPTION OF RADIOSODIUM FOR DIFFERENT CULTURE TEMPERATURES

temperature at 25°C. in both instances. Since radiosodium has a half-life of only 14.4 hours, the observed results given in curves *A* and *B* should be corrected for beta-ray decay. When this correction is made the actual uptake is shown by curves *A'* and *B'*. The data indicate that the rate of absorption is nearly doubled for a ten-degree rise in temperature. In general individual plants will check each other quite closely; however, it is always necessary to use more than one plant since individuals are often found in which the uptake may deviate from the average by a factor of 2.

The absorption of sodium and phosphorus by five-weeks-old corn seedlings, which had been grown for one month in a nutrient-deficient medium, was compared with that of normal two-weeks-old seedlings. The first group of plants had developed the prolific fibrous root system characteristic of nitrogen deficiency. When radioactive NaCl and K_3PO_4 were added to the culture solution, absorption was negligible even after several days. In order to determine whether this failure to absorb resulted from some localized defect or was due to some general condition of the plant, the root system and stem were excised section by section until absorption could be detected. In every case a point was found, either at the base of the roots or in the stem, above which the uptake was very nearly the same as that in the normal two-weeks-old seedlings. Microscopic examination of the excised sections showed a fibrous cellulose structure which was doubtless responsible for the low absorption.

STUDIES ELSEWHERE

Valuable contributions to the isotope technic have been made by Jenny[12] and his co-workers at the University of California. They have studied many of the factors influencing the elimination of radiosodium and radiopotassium from barley roots in which appreciable quantities have been absorbed; the effect of contact between the soil colloids and the roots on cation interchange has been investigated in detail. The results show that for equal amounts of cations in the nutrient media, the elimination is markedly greater in clay suspensions than in single salt solutions and negligible in distilled water; the outgo of radioactive potassium from the plants increases with the concentration of the nutrient media and with the time of contact. Exchange reactions between the culture solutions and the roots are of particular interest. Plants with high potassium levels and plants at low temperatures show no net absorption of potassium, although radiopotassium is actually taken up; this indicates the presence of an exchange of isotopes in the culture with the potassium in the roots.

Exchange processes within the plant have received considerable attention at Hevesy's laboratory.[13] It has been shown that P^{32} atoms within the stems and leaves are in a mobile state and that during the growth of the plant a continuous interchange of phosphorus atoms takes place between different leaves. Biddulph[14] finds this interchange to occur primarily between phosphorus atoms remaining in the water-soluble state.

An extremely important exchange study has been made by Vickery and Schoenheimer[15] using buckwheat plants grown in a culture medium containing N^{15} in the form of NH_4Cl. At the end of 47 hours the proximate components of the leaf, stem, and roots were separated and upon analysis were found to contain N^{15}, indicating that the physiologically active protein of the cells enters into reaction with the simple nitrogenous substance in the sap and that a continuous exchange takes place between the nitrogen of the amino acids combined in the protein and nitrogen in the sap. Similar findings in animal tissues have been reported. The dynamic nature of the chemical compounds composing living matter is directly indicated by this interchange of heavy nitrogen isotopes.

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[12] JENNY AND OVERSTREET, *J. Phys. Chem.*, **43**, 1185 (1939); *Soil Sci.*, **47**, 257 (1939); *ibid.*, **48**, 9 (1939).

[13] HEVESY, LANG, AND OLSEN, *Nature*, **139**, 149 (1937).

[14] BIDDULPH, *Plant Physiol.*, **15**, 131 (1940).

[15] VICKERY, PUCHER, SCHOENHEIMER, AND RITTENBERG, *J. Biochem.*, **129**, 791 (1939).

While many of the results mentioned above could have been obtained by conventional methods, the radioactive isotope technic possesses a number of decided advantages. Since measurements can be made under controlled conditions without injury to the tissue, an entire series of observations can be obtained from an individual plant. A quantitative estimate of the material absorbed in any section of the plant can be made in a few minutes; these measurements are independent of the initial constituents present in the plant. It is possible to determine the rate of absorption and distribution of the element in question in each section of the plant. Exchange between various sections of the plant and between the plant and culture medium can be followed quantitatively. In general the isotope technic results in a material saving in the number of plants required as well as in time and labor.

While the results just mentioned illustrate the usefulness of the isotope technic they do not show its greatest possibilities. Unquestionably the most far-reaching gains are to be made in tracing the course of metabolic reactions within the cell. Numerous investigations of this character have been undertaken with animal tissues; as yet only a limited application has been made to plant problems. It has been suggested that the fixation of nitrogen in leguminous root nodules results from a series of reactions involving $N_2 \rightarrow$ hydroxylamine $\rightarrow$ oxime of oxalacetic acid $\rightarrow$ aspartic acid, the entire process requiring several hours. By using nitrogen containing N^{15} it should be possible to identify the various steps in the reaction mechanism. Heavy carbon, or preferably the long-lived radioactive isotope prepared from heavy carbon, may facilitate the solution of such problems as photosynthesis, translocation, carbohydrate and fat formation, and investigations involving the metabolic processes within the plant which have so far defied solution by conventional methods.

The writer is indebted to Dr. M. A. Tuve of the Carnegie Institution of Washington for the radioactive material used in the various experiments.

A Modern Visit to Liebig's Laboratory[1]

CHARLES J. BRAND *The National Fertilizer Association, Washington, D. C.*

GIESSEN, the chief city of upper Hesse, is located in the fertile valley of the river Lahn, thirty-four miles north of Frankfort-am-Main. It is about the size of Ann Arbor, but its State University (Landesuniversitaet) founded in 1607 is very much smaller than the University of Michigan, having less than 2000 students in residence. The small size of the University is due in part to the fact that there are four universities, beginning with Heidelberg (1386) on the south, Frankfort (1914), Giessen (1607), and Marburg (1527), in a distance of 104 miles.

It was to this town and to this university that Justus Liebig came in 1824 at the age of 21 as professor extraordinarius in the faculty of philosophy, to do teaching and research work in chemistry.

Collegiate intramural administrative problems existed in educational institutions then as they do now. The Grand Duke of Hesse had named Liebig on Alexander von Humboldt's recommendation without the usual submittal to an examination by the faculty. In consequence, Liebig was not made as welcome as he otherwise would have been. The trouble was due chiefly to the facts that there was already a professor ordinarius (Dr. W. L. Zimmerman) on the faculty; that the facilities for scientific research in chemistry were very meager, and that, with the teaching functions, they had already been assigned to Zimmerman. Furthermore, the funds available were so small as almost to forbid providing a suitable laboratory.

Liebig was filled with ideas about the paramount importance of the laboratory as a teaching facility. It is worth remembering that his fostering of the laboratory method of teaching played an important part in establishing teaching laboratories in chemistry throughout the world. Liebig is as distinguished for his services to education as for his work in the furtherance of pure and applied science. When, at the conclusion of his studies at Bonn and Erlangen, he had taken his doctor's degree, he found in all Europe only two chemistry departments that seemed to him supplied with the facilities for study and research that he sought. They were those of Gay-Lussac in Paris, and of Berzelius in Stockholm.

In 1822, at the age of nineteen, Liebig betook himself to Paris where he had the good fortune to meet von Humboldt for the first time. Humboldt was so attracted to him that he became his sponsor and induced Gay-Lussac to accept him as an advanced student.

The uphill row Liebig had to hoe at Giessen after his appointment on May 26, 1824, because the chemical department already had a head, is indicated by the fact that it was not until November 7 that a lecture room became available to him. Twelve students began their work with him on that day.

It is an interesting sidelight on the students of the time, their nationwide conduct culminating in 1848 in the Student's Rebellion, that they were in constant turmoil with the local military garrison. Finally, to

[1] Presented as part of the Liebig Symposium before the Divisions of Fertilizer Chemistry, Agricultural and Food Chemistry, and History of Chemistry at the one-hundredth meeting of the A. C. S., Detroit, Michigan, September 10, 1940.

end the constant disorders, the government moved the troops to Worms, thus releasing their barracks, which were assigned to the University. One of the old guardrooms in the second story of what is now the Liebig Museum Building was Liebig's first lecture hall.

In 1826 matters changed considerably. Professor Zimmerman died suddenly, and the first-floor rooms of the old guardhouse were assigned to Liebig for his laboratory and lecture auditorium, and he was given permission to convert the old lecture room in the second story into a living room.

LIEBIG'S LECTURE ROOM AT GIESSEN
Note opening (behind lecture table) leading into the main laboratory

From 1826 until 1832, Liebig got along with three rooms; one he used for his laboratory, another for his lecture auditorium, and the third for his living room. In the latter year, he obtained permission to convert a woodshed behind the laboratory into an additional laboratory, and the old auditorium into a heated balance room and a private laboratory. It was not until September, 1835, that the changes were made which he had requested and had been promised in 1833.

A few comments on the salaries of scientific workers in that far-off day will be of interest. When Liebig was appointed in 1824, his salary was 300 gulden, about $105.00 yearly. When, after Zimmerman's death in 1826, he was appointed regular professor, his pay was 800 gulden. He continued to receive the same rate of pay until 1835, when he was given an assistant. This was practically an increase in pay, as up to that time he had been compelled to pay his assistant out of his own pocket. In 1837, his salary was raised to 1650 gulden, because the University of St. Petersburg sent him an urgent invitation to join its faculty. In 1841, he was given a further raise to 3200 gulden when the University of Vienna invited him to its Chair of Chemistry. In addition, von Liebig was given some additional allowances which were a great help to him, for he had long been paying the operating deficit of his department out of his own pocket.

To return again to his laboratory, its size was increased for the last time in 1839 at a cost of 12,000 gulden. This gave the Institute of Chemistry twice its previous floor space. The facilities now included a good-sized auditorium, a large adjacent working laboratory, a small lecture room for the beginners, a balance room, and a room for the library and the air pump. This was the period during which students from all parts of the world streamed into Giessen to do advanced work in agricultural and physiological chemistry. The auditorium was altogether too small; it had 60 seats and there were never less than about 120 taking the lectures. Those who sat in the front of the room had to occupy benches and other improvised seats and put their ink pots on the experimental table.

In 1852 Justus von Liebig, now a baron, a chevalier of the Legion of Honor, and a holder of many other titles of distinction, accepted the invitation to go to the University of Munich, and his private assistant, Heinrich Will (1812–82), was named ordinary professor of chemistry at Giessen, chief of the laboratories, and Liebig's successor.

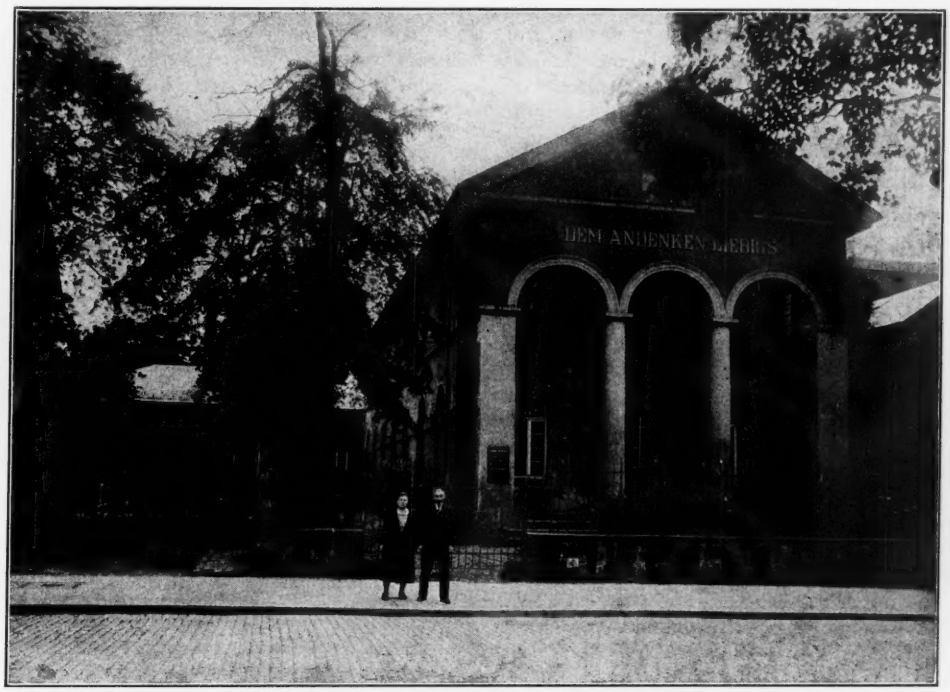
Prior to Liebig's time, practical teaching in the chemical laboratory existed nowhere. He had to develop his own methods of teaching and demonstrating and spent an almost endless amount of time in devising methods of interesting his pupils and spurring their zeal, using practical experiments, recitations, and examinations. Thus Liebig founded the first school of chemistry, and the modest laboratory that he opened in 1824 was the forerunner of great chemical institutes

that now exist in all important universities. He himself in his brief autobiography said:

"We worked from break of day to the sinking night. Diversions and amusements there were none in Giessen. The only complaints, and they were heard again and again, were those of the janitor (Aubel) who, at night when it was time to clean up the laboratories, found it impossible to get the workers to clear out so that he could do his duty."

those of his contemporaries, together with an interesting collection of books and pictures.

The curator of the museum, a woman, obligingly shows strangers through the various laboratories and other rooms and tells them as best she can about Liebig's work as teacher, research worker, writer, and international figure. She may mention his work on explosives, beet sugar, phosphoric acid, potash, nitro-



FRONT OF LIEBIG LABORATORY AND MUSEUM IN GIESSEN

It was my privilege, in July, 1937, while attending the National Congress of German Chemists on the Fiftieth Anniversary of the Union of German Chemists at Frankfort, to visit Liebig's old laboratory. It is kept up by a foundation, supported by a small endowment and free-will gifts, which was organized in 1910, when a small group of scientific and technical workers determined to preserve this renowned laboratory. In due time efforts were instituted to put the building in proper repair and to begin the collection of old pieces of apparatus, utensils, and other items which had been scattered to the winds. The efforts were successful; condensers, absorption apparatus, air pumps, ovens, old-fashioned retorts, and many other interesting objects have been collected and put in place.

The visitor will find in the Museum building the oldest of the laboratories with its adjacent rooms; von Liebig's private laboratory and its work room; the large analytical laboratory with its lecture hall, the pharmaceutical laboratory, and a collection of plastics, documents, writings in von Liebig's own hand, and in gen, fermentation, meat extracts, and many other subjects. Usually, I think, emphasis is laid on the fact that first of all Liebig was a great teacher who, in this particular old laboratory building, laid the foundation of our present laboratory method of instruction and of modern research in organic chemistry.

The memorial laboratory building with the words, "In memory of Liebig," above its façade, has a somewhat classic front with a side entrance. It is kept in an excellent state of repair. In the public park near by there is a fine marble statue that has been erected in Liebig's honor.

To one interested in all phases of agriculture and agricultural chemistry, the visit to Giessen is an inspiration, and reminds one that perhaps Liebig's greatest service to humanity was to teach all who came under his instruction the necessity for distinguishing opinions from facts.

In this day of world-wide turmoil and war, we could well go back to much of von Liebig's philosophy and teaching.

Steric Hindrance in Organic Solids

B. S. BIGGS

Bell Telephone Laboratories, New York City

IN A recent paper from these laboratories[1] there was presented dielectric evidence that molecular rotation occurs in the crystals of certain polysubstituted benzene derivatives.

The molecules of most substances, on passing from the liquid into the solid state, lose both their translational and rotational motion and assume fixed positions in the crystal lattice. It is a definitive requirement of the solid state that translational motion must be lost, but it is now clear that molecules in a crystal do not necessarily lose their rotational motion provided that their own peripheries are smooth enough—that is, that the fields of force are small and regular enough that neighboring molecules do not block each other. In other words, if all molecules fell in the classes of perfect spheres,[2] perfect rods,[3] or perfect discs, then all molecules would rotate to some extent in the crystal lattice. The fact that relatively few molecules have the requisite symmetry has tended to obscure this generalization. The rotation here referred to is the same as that ordinarily considered to be characteristic of the molecules of liquid, except that in the case of flat molecules such as most benzene derivatives, this rotation in the crystal lattice is undoubtedly about the axis perpendicular to the plane of the ring.

The method by which rotation is detected is the measurement of the dielectric constant. When a homogeneous organic compound exhibits a dielectric constant much greater than the square of its refractive

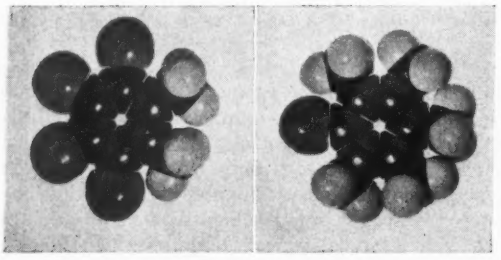


FIGURE 1

index, it does so by virtue of the ability of a dipole to rotate under the influence of an applied field. Hence the method is limited to polar compounds, although non-polar compounds which meet the symmetry requirements undoubtedly rotate also. The details of the measurements are described in the previous paper.

The object of this paper is to discuss the limiting deviations from perfect symmetry which will still permit compounds of the substituted benzene class to rotate in the solid state. Figure 1 shows photographs of scale models of two hexa-substituted benzenes in which the substituents are chlorine and methyl groups, and illustrates their almost perfect circular symmetry. Figure 2 represents these same molecules in an idealized form in which the methyl groups are considered to be

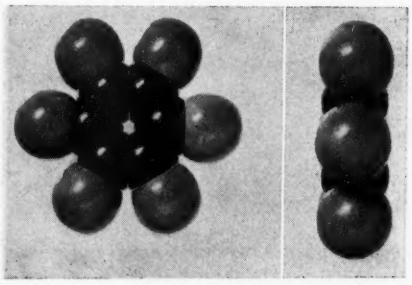


FIGURE 2

spheres of about the same diameters as the chlorine atoms. The various ways in which such molecules can depart from perfect symmetry may be conveniently divided into three classes under the headings: (1) indentations of the periphery, (2) protrusions from the periphery in the plane of the disc, and (3) protrusions from the plane of the disc. Many compounds, of course, deviate in more than one of these ways.

MOLECULES WITH INDENTED PERIPHERIES

The examination of a number of penta-substituted benzenes has led to the conclusion that one indentation of the periphery equivalent in size to the space occupied by one substituent does not prevent the rotation of the molecule in the temperature range immediately below the melting point. Tetrachlorotoluene, trichloro-*o*-xylene and trichloro-*m*-xylene, all of which melt between 90° and 100°, rotate freely (*i. e.*, as freely as they do in the liquid state) down to about 20°, and then rotation ceases abruptly. They differ in this respect from the compounds of the more perfect disc type, which rotate down to lower temperatures and finally lose the ability to rotate, gradually rather than abruptly. This is interpreted as meaning that when the molecules possess a relatively large amount of energy, as they do at high temperatures, they are able to overcome the interlocking tendency of the indentations, but as the energy decreases interlocking sets in and immediately spreads throughout the mass. It is interesting that at this transition point there is a density

[1] WHITE, BIGGS, AND MORGAN, *J. Am. Chem. Soc.*, **62**, 16 (1940).

[2] BAKER AND SMYTH, *J. Am. Chem. Soc.*, **61**, 2063, 2798 (1939); WHITE AND BISHOP, *ibid.*, **62**, 8 (1940).

[3] BAKER AND SMYTH, *ibid.*, **60**, 1229 (1938).

change, in some materials amounting to about eight per cent, in keeping with the fact that an individual molecule would require more space for the rotating than for the interlocked form. Figure 3 shows the

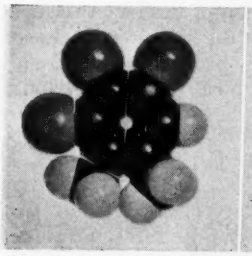


FIGURE 3

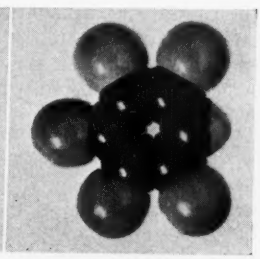


FIGURE 4

usual model of trichloro-*o*-xylene and Figure 4 represents this type of molecule with the methyls represented by spheres. The hydrogen atom shown in this idealized model is smaller than the usual hydrogen model, and probably more nearly represents the relative size in these compounds in the solid state. Further proof of the steric nature of this effect may be found in the fact that when a compound with one indentation, such as trichloro-*o*-xylene, is diluted with fifteen per cent or more of one of the perfect discs, such as *o*-dichlor tetramethyl benzene, rotation continues at temperatures much below the normal transition and finally stops gradually as does that of the perfect disc. Presumably the presence of a small amount of the perfect disc keeps the indentations far enough apart that interlocking is prevented.

Of the compounds containing four substituents, all of which are either methyl or chlorine groups, none has been found to rotate in the solid state. These include 1,2,3,4-tetrachlorobenzene, (m. p. 41°), in which there is only one indentation (but a large one); and 4,6-dichlor-*m*-xylene (m. p. 68°), 4,5-dichlor-*o*-xylene (m. p. 76°), and 2,4,5-trichlorotoluene (m. p. 82°), in each of which there are two indentations *para* to each

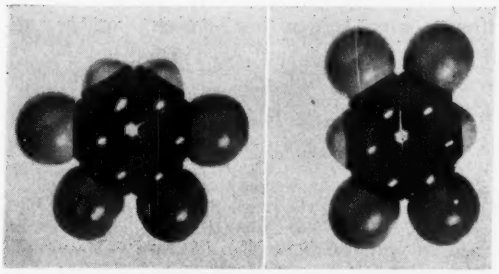


FIGURE 5

other. Idealized models of these compounds are shown in Figure 5. The tetra-substituted benzenes of this type with the two indentations *meta* to each other are almost all liquids at room temperature and have not been measured.[4] As far as the data are available they point to the conclusion that while one small indentation leaves rotation possible, either one large indentation or two small ones will permit rotation to take place.

MOLECULES WITH PROTRUSIONS IN THE PLANE OF THE RING

Among compounds containing protrusions out of the circle but in the plane of the ring are chlorobenzene, *o*-dichlorobenzene, cyanobenzene, etc., where the original symmetry of the benzene ring has been destroyed by the protruding substituent. No mono-, di- or trisubstituted benzene of this type (Figure 6) has been found to rotate in the crystalline solid. Hexa-substituted benzenes which represent this class and this class only are rare, since most groups which extend more than one atom away from the ring, such as the ethyl group, also extend out of the plane of the ring. Pentamethyl cyanobenzene, whose scale model is shown in Figure 7, is the only one which has been

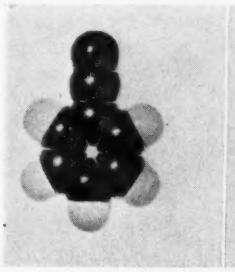


FIGURE 6

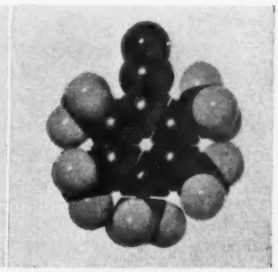


FIGURE 7

measured here. This compound is of particular interest because its behavior seems to fall between that of the penta-substituted or transition type molecule and the hexa-substituted perfect disc type. The molecule rotates down to relatively low temperatures and the rotation begins to decrease in the manner of the perfect discs, when finally a transition sets in and rotation ceases. This result seems, to indicate that the deviation from perfect symmetry found in this molecule is slightly less than the maximum which would still permit rotation. If a compound were available which was similar to this, but which had a slightly larger protrusion, it might be expected to be a typical transition compound.

MOLECULES WITH PROTRUSIONS OUT OF THE PLANE OF THE RING

The third class of compounds is well illustrated by nitro pentamethyl benzene, *o*-dinitro tetramethyl benzene, ethyl pentachlorobenzene, and *o*-dinitro tetraethyl benzene. The geometric projections of these compounds in the plane of the ring all deviate from per-

[4] One exception is 2,4,6-trichlorotoluene, but the polarity of this molecule is so slight that the evidence is not clear-cut.

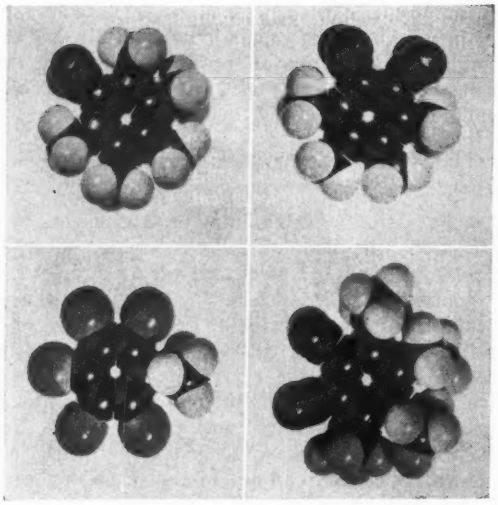


FIGURE 8

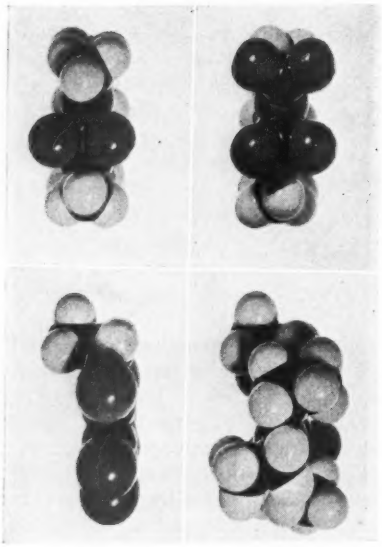


FIGURE 9

fect discs no more than does pentamethyl cyanobenzene, yet the only one of the group which rotates is *o*-dinitro tetramethyl benzene and that only above 154°. Figure 8 shows the models of these compounds viewed from the axis of the ring, and Figure 9 along the plane of the ring. The explanation of the fact that none of these compounds rotates in the solid state below 154° must lie in the fact that they protrude out of the plane, and these protrusions must block each other enough to stop rotation. The importance of the steric factor is

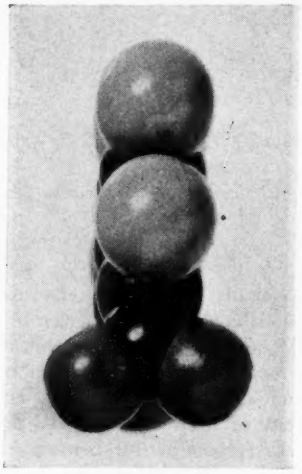


FIGURE 10

especially clearly illustrated by ethyl pentachlorobenzene, which does not rotate below its melting point, 58°, whereas its methyl homolog rotates down to about −60°. The protrusion of the nitro group in nitro pentamethyl benzene is shown more clearly in Figure 10, in which the methyl groups are shown as spheres. The fact that *o*-dinitro tetramethyl benzene rotates above 154° does not necessarily mean that its symmetry is greater than that of nitro pentamethyl benzene, because the latter happens to melt at that temperature. Many compounds, no doubt, lie close enough to the borderline in symmetry that if their melting points were a few degrees higher rotation might occur.

Eminent Men of Science Living in 1807–8

(*Continued from page 205.*)

Thomas Thomson—IRVINE, "Scotland's contribution to chemistry," **7,** 2813 (1930); DAINS, "John Griscom and his impressions of foreign chemists in 1818–19," **8,** 1309 (1931); WEEKS, "The discovery of the elements. VII. Columbium, tantalum, and vanadium," **9,** 871 (1932); ATKINSON, "The atomic hypothesis of William Higgins," **17,** 8 (1940).

James Watt—IRVINE, "Scotland's contributions to chemistry," **7,** 2822 (1930).

William Hyde Wollaston—DAINS, "John Griscom and his impressions of foreign chemists in 1818–19," **8,** 1293 (1931); WHITE AND FRIEDMAN, "On the discovery of palladium," **9,** 241 (1932); WEEKS, "The discovery of the elements. VIII. The platinum metals," **9,** 1023 (1932); WEEKS, "Some scientific friends of Sir Walter Scott," **13,** 505 (1936); FERGUSON, "Bergman, Klaproth, Vauquelin, Wollaston," **18,** 5 (1941).

What's Been Going On

(*Continued from page 202.*)

repeated laundering. Under the trade name of Ethocel, it bids to take its place among the synthetic fibers.

Among other synthetic products that are edging their way into this field are synthetic rubber filaments such as Lastron and the polymer of vinylidene chloride. The latter is produced by the Dow Chemical Company, and has a molecular configuration represented by:

$$(\cdot CH_2 \cdot CCl_2 \cdot CH_2 \cdot CCl_2 \cdot CH_2 \cdot CCl_2 \cdot)_n$$

This product has practically the same refractive index as that of water, is very strong and resistant to the reaction of chemicals, and is finding use for leaders and fishing nets as well as many other applications. —ED. F. DEGERING

The Polarographic Method of Analysis

IV. Fundamentals of Qualitative Analysis

OTTO H. MÜLLER

Department of Anatomy, Cornell University Medical College, New York City

IN ORDER to produce a continuous flow of current through an electrolytic cell, a certain minimum voltage, the decomposition voltage, must be applied. In other words, the two electrodes to which the voltage is applied must be charged up, or polarized, to potentials different from those which they naturally assume when submerged in the electrolyte. Two methods are available for the measurement of such polarization potentials: in the first method, most generally used, the potentials of the working anode and cathode are measured separately with a potentiometer against a third, reference electrode of known potential; in the second method, used extensively in polarography, one of the active electrodes is a non-polarizable electrode with a large surface and serves as reference electrode for measuring the polarization of the other, small, active electrode. It has been found that such potentials depend not only on the nature and concentration of the electro-active material but also on the type of electrode. Applying this knowledge, investigators found satisfactory electrodes and determined suitable voltages for the electrolytic separation of many metals and thus developed the electrolytic method of analysis.[1]

As has been stated before, polarography is also an electrolytic method but one in which only a minute fraction of the solution is electrolyzed so that the solution as a whole remains essentially unaltered. Here the voltage necessary for this electrolysis at the smaller electrode serves for qualitative analysis. It usually indicates the composition of only that small part of the solution which is in immediate contact with the electrode. It is seldom constant because, whenever current flows, this composition changes. Therefore the potential obtained polarographically and that obtained by the potentiometric method are identical only in exceptional cases. Under favorable conditions the polarographic potentials of most metallic and many organic reductions differ measurably from one another and can be used to identify these substances. Often, however, the reduction potentials of several substances present in the same solution differ but little. Suitable reagents must then be added, which by forming complexes with the reactants will separate their reduction potentials. This failing, a preliminary separation of the components by chemical means becomes necessary before the polarographic analysis. To date no general procedure for the analysis of an unknown has been worked out but many detailed instructions for special analyses are available. With a clear understanding of the underlying principles, every chemist will be able to use the polarographic method for some of his problems along with the diverse technics of general qualitative and quantitative analysis.

This paper will be devoted to a consideration of the significance of the polarographic wave and the conditions responsible for the observed potentials. This has become possible since the publication of a most important paper by Heyrovský and Ilković[2] in which the so-called "half-wave potential" was suggested for characterizing polarographic oxidations and reductions. Because the potentiometric and electrolytic methods merge in the polarographic method,[1] a part of this paper will be devoted to an explanation of the terms which must be applicable to all. It has been my experience that the greatest problem for the novice in polarography is the correlation of electrolysis with measurements of electromotive force, since both have been taught to him as separate subjects. It is my hope that this paper will show the interrelation of these subjects and call attention to the prevailing difficulties in terminology.

TERMINOLOGY

As was stated above, the minimum voltage necessary to cause a continuous flow of current through the electrolytic cell is the decomposition voltage. This is often also called the decomposition potential, a term which is indeed confusing and must be considered a misnomer caused by the following complex definitions.

Potential is an energy level defined as "a characteristic of a point in an electric field or circuit indicated by the work necessary to bring a unit charge to it from infinity," or "the degree of electrification as referred to some standard, as that of the earth." It is analogous to "level" in mechanics and hydrostatics.

Electromotive Force (E.M.F.) is defined as "the force which by reason of difference in potential produces electric currents," or "difference of potential." It is analogous to "pressure" in hydrostatics.

Volt is the unit of electromotive force.

Voltage is defined as (*a*) the electric potential and (*b*) the potential difference, or E.M.F., expressed in volts.

This last definition is responsible for most of the existing confusion because both the potential and the difference in potential (E.M.F.), which are not the same thing at all, are expressed in volts. Obviously, in electrolyses we are not dealing with a decomposition potential which should be referred to some standard, but with that difference in potential between two electrodes which is necessary to bring about a decomposition. The term "decomposition potential-differ-

[1] J. CHEM. EDUC., **18**, 65 (1941).

[2] *Collection Czechoslov. Chem. Commun.*, **7**, 198 (1935).

ence" would therefore be more appropriate. It would avoid confusion if the term "voltage" were reserved for differences in potential expressed in volts, or even better, if it were reserved for "applied E.M.F.," often called "bath-voltage," which is the quantity that is always measured directly. In the remaining discussions voltage will be used in the latter sense.

According to the above definitions, *a potential refers to a single electrode or half-cell, while an E.M.F. always has to do with the difference in potential between two electrodes or half-cells.* A "current–voltage" or "current–applied voltage" curve is therefore a curve in which the E.M.F. applied between the two electrodes of an electrolytic cell is plotted against the current. A "current–potential" curve (sometimes perhaps misleadingly called "current–applied potential" curve) on the other hand represents the potential change of one electrode or its polarization during an electrolysis, plotted against the current.

Many attempts have been made to obtain a null electrode, *i. e.*, an electrode with absolute zero potential to which other electrode potentials could be referred. These were finally abandoned, and the hydrogen electrode was selected instead as an arbitrary standard. Its potential at atmospheric pressure and unit activity of hydrogen ions is taken as zero at all temperatures. Potentials referred to this standard are usually designated by E_h. In practice, it is more convenient to measure potentials against the saturated calomel electrode; the potential is then designated by $E_{S.C.E.}$ The potential of such calomel electrodes at 25°C. is 0.246 volt more positive than the standard hydrogen electrode so that $E_{S.C.E.}$ values can be easily converted to E_h values by adding this difference.

In measurements of electrode potentials the utmost care is taken to avoid the flow of current. If this precaution is neglected, the electrode may become polarized, *i. e.*, show a potential different from that which it has under equilibrium conditions. This polarization may be due to changes in the electrode itself or in the surrounding layer of solution; it can be diminished and often prevented by stirring of the solution or by increasing the concentration of the electro-active material (depolarizer) which "poises" the electrode, *i. e.*, prevents polarization.

Let us now consider two half-cells in which both electrodes are well poised, such as a copper electrode dipping into a copper sulfate solution and a zinc electrode dipping into a zinc sulfate solution. If we connect these half-cells by a porous diaphragm or some other liquid junction we have the familiar Daniell cell. This is a *galvanic* cell, *i. e.*, a cell in which chemical reactions at the electrode will proceed spontaneously to produce electric energy if the two metals are connected by a conductor. The zinc will be oxidized and go into solution as zinc ions, there to displace copper ions which in turn will be reduced to the metallic state and deposited on the copper electrode. The zinc may therefore be considered the anode and the copper the cathode.[1] However, it is more common to look at the electrodes as points from which energy of the galvanic cell may be tapped. The zinc is then the negative and the copper the positive electrode, because electrons flow *through the external connections* from the negative to the positive electrode. This agrees with the terminology used throughout these papers concerning the sign of single electrode potentials; the zinc electrode is more negative than the copper electrode. Another exactly opposite terminology is, of course, equally possible and is used by many. In this, the transfer of electrons *through the electrolyte* is considered of first importance, wherefore the electrode potentials have the opposite signs.

Since the two electrodes are well poised and of large capacity it is possible to measure their potential difference—the voltage of the cell—by means of a voltmeter, although current will flow and some of the energy of the galvanic cell will be consumed in this process. A more accurate result would be obtained by applying from some outside source a known counter E.M.F. which could be made to balance exactly the E.M.F. existing between the two electrodes so that no current flows. If the applied E.M.F. exceeds that existing between the two half-cells, the electrode reactions are reversed and the current will flow in a direction opposite to that observed during the spontaneous discharge of the galvanic cell. Under these conditions, the copper electrode is anode and the zinc electrode is cathode, and we now have an *electrolytic* cell in which electric energy is consumed to produce a chemical reaction. Now, the potential difference existing between the two electrodes is the counter E.M.F. If the current is kept small enough, neither of the electrodes becomes polarized regardless of the direction of current. This, of course, is a somewhat unusual case because the reactions at both electrodes are reversible. It serves to demonstrate that there is little difference between electrolytic and potentiometric phenomena. One difference is that in most practical electrolyses a marked polarization of the electrodes occurs or that the reaction on at least one electrode is irreversible. In potentiometry, as a rule, only reversible reactions are considered, although in recent years some irreversible reactions have also been investigated.

In any case the following variation of Ohm's law must hold:

$$V = E_1 - E_2 + IR \qquad (1)$$

where V is the applied "voltage," E_1 and E_2 the potentials of the two electrodes, I the current, and R the resistance. E_1 is the potential of the cathodically polarized electrode, *i. e.*, the electrode connected to the negative side of the potentiometer. This corresponds to the negative electrode in a galvanic cell. I is positive if such a cell reacts spontaneously.

We can see from this that if the applied voltage V exceeds the opposing decomposition voltage $(E_1 - E_2)$ an increase in current must result that is inversely proportional to the resistance. The foregoing considerations may be clarified by the following ex-

periments which can be carried out with the apparatus described in Part II of this series.[3]

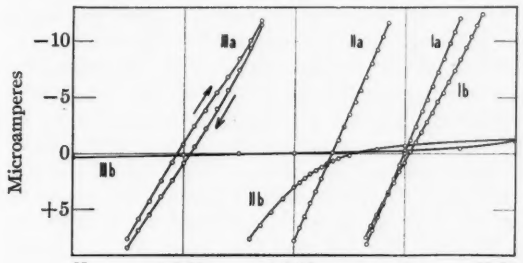


FIGURE 1.—CURRENT–VOLTAGE CURVES

Experiment 1.—Prepare a saturated calomel half-cell with a mercury surface of about 15 cm.². This electrode is used as reference standard in this and the following experiments and is connected to the half-cells studied by means of an agar bridge.

In this experiment use a bridge saturated with potassium chloride. Then, with the vessels open to air, electrolyze the following:

(I) A solution saturated with potassium chloride and with calomel.

(II) A solution of approximately *N* potassium chloride saturated with calomel.

(III) A solution of 0.1 *N* potassium nitrate.

As electrodes use (*a*) a layer of mercury of about 7 cm.², and (*b*) the dropping mercury electrode. (Since we use a saturated potassium chloride bridge, some potassium chloride will diffuse into the test solutions. Solution II will therefore be slightly more concentrated than prepared and solution III will represent a dilute potassium chloride solution which has been made conductive by potassium nitrate.) Apply potential differences between these half-cells and the reference electrode, increasing and decreasing in steps of 3 millivolts starting from zero. This can be done without changing connections if use is made of the "anodic and cathodic polarization" described previously.[3] In the case of solutions II and III we actually have galvanic cells and a large current will flow unless it is opposed by a counter E.M.F. This has to be remembered when pressing the tap key of the apparatus.[3] To protect the galvanometer it is best to use the shunt in position No. 2 or 3 until an approximate balance is obtained. Repeat these experiments several times in quick succession to test for reproducibility. In the case of solution III, the potentials of the layer electrode will show a drift; for plotting use the values obtained after 30 seconds. Observe the currents with the galvanometer shunt at position No. 4.

If the observed current is plotted against the applied voltage we obtain the "current–voltage" curves shown in Figure 1. When voltage is applied to two large well poised electrodes (curve I*a*) the current I increases linearly with the applied voltage in a ratio that is determined by the resistance R of the circuit, ($E/I = R$) just as if the voltage had been applied to a fixed metallic resistor. Neither electrode is polarized as long as the current stays small. Since the half-cells are identical they have the same potential E, and no current flows when no outside voltage is applied. From this curve we can calculate the resistance of the circuit using Ohm's law and find it to be 2500 ohms. The fact that both of the electrodes can serve as anode or cathode without being polarized shows that we can use either of them as reference electrode for the study of other electrodes up to similar currents.

The results obtained with the dropping mercury electrode (curve I*b*) differ in two points from those plotted in curve I*a*. First, at zero applied voltage a small current flows showing that the potential of the dropping electrode must be more negative than that of the calomel half-cell by about 3 millivolts. Second, there is a difference in slope which must be due to polarization of the dropping mercury electrode, because the increase in resistance caused by the flow of mercury through the fine capillary is only about 50 ohms and could not change the curve significantly. If we plot the corresponding "current–potential" curves (Figure 2, I*a* and I*b*) by applying equation (1) to the data used in Figure 1, the polarization of the dropping mercury electrode is clearly shown, and the constancy of the potential of the layer electrode is demonstrated by a line parallel to the y ordinate.

The results obtained with the layer electrode in solution II (Figure 1, curve II*a*) demonstrate what has been described above in connection with the Daniell cell. At first, we have a galvanic cell, the E.M.F. of which we oppose by applying a counter E.M.F. from the potentiometer. We reduce the current linearly with an increase in the applied voltage until we reach a point where no current flows. The applied E.M.F. is then equal to the E.M.F. of the cell, in this case 39 millivolts. Since one half-cell is a saturated calomel electrode, the potential of the other half-cell must be $E_{S.C.E.} = +39$ millivolts. As we increase the applied voltage still further we change the galvanic cell into an electrolytic cell; the current, now of opposite direction, increases linearly with the applied voltage. The E.M.F. of the galvanic cell is now the counter E.M.F. The polarization of the electrode remains negligible throughout, as may be seen from curve II*a* in Figure 2.

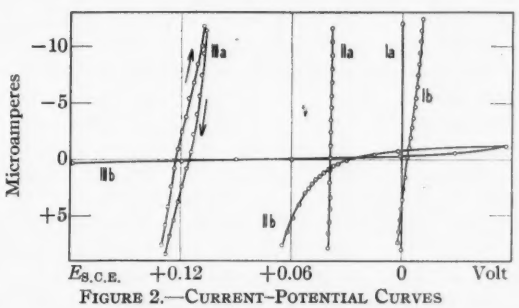


FIGURE 2.—CURRENT–POTENTIAL CURVES

In the same solution II, the dropping mercury electrode shows a marked polarization even when only very little current is flowing (Figure 2, curve II*b*). This polarization is greater when the electrode reaction is cathodic than when it is anodic. The important point to note here is that there exists no visible effect of time or of previous polarization on the polarization of the dropping mercury electrode. It seems to be

[3] J. CHEM. EDUC., **18**, 111 (1941).

polarized instantaneously to the fullest extent. This is further amplified by the experiments with solution III, where the layer electrode shows the effects of time and direction of polarization (Figure 2, curve III*a*), while the dropping mercury electrode is fully polarized at every instant (Figure 2, curve III*b*). The polarization observed here is due to the fact that no calomel is present and that the chloride ions are quickly depleted around the electrode in the formation of calomel during the anodic dissolution of mercury. Chloride ions are depolarizers for the anodic reaction, while calomel is the depolarizer for the cathodic reaction. The current obtained with the dropping mercury electrode in solution III is very small and is of the nature of a residual current as described in Part III.[4] The "current–potential" curve (Figure 2, III*b*) is therefore almost identical with the "current–voltage" curve (Figure 1, III*b*) because *IR* becomes negligible. This feature of complete and instantaneous polarization makes the dropping mercury electrode so well suited for polarographic studies. The presence of measurable quantities of depolarizers makes itself known immediately by an increase in current above the residual current. The potential at which these depolarizers act serves for qualitative analysis; the degree to which they prevent perfect polarization by producing a flow of current serves for quantitative analysis.

Although, in general, every metal has a definite potential, the potential cannot be measured when the metal is hanging in air because any measuring device will certainly polarize it. The current necessary for this polarization is extremely small. For instance, if two identical metallic electrodes are kept in air, we can apply a difference in potential between them and thus polarize or charge them. A negligible current will flow until the applied voltage is several thousand volts, when free electrons will leave one of the electrodes and pass to the other, even through air. In aqueous solution it is impossible to charge or polarize metallic electrodes to very high potentials because a depolarizer is always present, coming from water or from the dissolved salt. The situation is but little improved if the metal, *e. g.*, platinum or mercury, dips into a solution of pure potassium nitrate. If extreme care is taken that no current flows, the potential of these electrodes can be measured. Such a potential is not reproducible because it is influenced by immeasurable traces of gases and salts dissolved in the solution or adsorbed on the electrode. The only potentials which are significant are those which are reproducible and which are due to the electrode reaction of a substance which can be analyzed and characterized. In general, this means that a concentration of electro-active material of 10^{-6} *M* is essential to poise an electrode.

Before the significance of the polarographic potentials was fully understood, arbitrary characterizations of reducible substances were used in order to make the polarographic method applicable to qualitative analysis. At first, that potential at which an increase of one millivolt in the applied voltage produced an increase in current of 10^{-8} amperes was called the deposition potential of the reacting substance. Later on, similar potentials were obtained from the intercepts of tangents of 45° or 35°16′ to the curve. The disadvantage of these empirical values lay in the fact that they varied with the concentration of the reacting substance and depended on such factors as drop-time of the electrode and galvanometer sensitivity. They had little relation to other thermodynamically significant potentials. It was a great step forward, therefore, when Heyrovský and Ilkovič[2] clarified the significance of the polarographic wave and suggested the half-wave potential for the characterization of the reacting material. This half-wave potential is independent of the concentration of the reacting material, the drop-time of the electrode, and the galvanometer sensitivity; it is, furthermore, closely related to the potentials obtained in potentiometric studies, as will be illustrated in the next chapter.

REVERSIBLE REACTIONS

The reactions which have made it possible to get a clear understanding of the processes at the dropping mercury electrode have all been reversible in a thermodynamic sense, as designated by the double arrows in the following equation:

$$\mathrm{Ox} + n\epsilon \rightleftharpoons \mathrm{Red} \qquad (2)$$

Here Red represents the same substance as Ox but differing by n in the number of negative charges (ϵ); together they form an "oxidation-reduction system." The electrode potential is a function of these components of the system and is given by the familiar equation:

$$E = E_0 - \frac{RT}{nF} \ln \frac{a_{\mathrm{Red}}}{a_{\mathrm{Ox}}} \qquad (3)$$

where R is the gas constant, T the absolute temperature, n the number of electrons involved in the reaction, F the Faraday, and a_{Red} and a_{Ox} the activities of the reductant and oxidant, respectively. E_0 is the electrode potential characterizing the oxidation-reduction system when the activities of oxidant and reductant are equal. To make this equation applicable to an electrode *during electrolysis* we have to use the activities of reactants as they exist at the electrode surface (henceforth called the interface), and not those existing in the body of the solution. For convenience we shall use the following less accurate form of equation (3):

$$E = E_0 - \frac{RT}{nF} \ln \frac{[\mathrm{Red}]_i}{[\mathrm{Ox}]_i} \qquad (4)$$

where the brackets indicate concentrations instead of activities and the subscripts i denote that we deal with the concentrations at the electrode/solution interface only. We can get an idea of these concentrations by considering a polarographic wave with a pure diffusion current, *i. e.*, one in which all factors influencing

[4] J. CHEM. EDUC., 18, 172 (1941).

the current except diffusion have been eliminated.[4] At the beginning of the curve no current flows, and the concentration of a reducible substance must be the same at the interface as in the body of the solution. As soon as the applied E.M.F. is large enough so that current flows, some of the reducible material (oxidant) at the interface is reduced and must be replenished from the body of the solution by means of diffusion. The reduction product (reductant) does not accumulate at the interface but diffuses away from it into the solution or into the electrode material. If the applied E.M.F. is increased to a point at which all oxidant reaching the interface is reduced, only the newly-formed reductant will be present. The current flowing under such circumstances is the diffusion current. Further increase in the applied E.M.F. will produce no further increase in current unless some other substance is reduced. A second wave indicating the simultaneous reduction of two components will then result. This can be treated like the first one. At the midpoint of a wave, one-half of all the oxidant which reaches the dropping mercury electrode during its lifetime is reduced to the corresponding reductant, so that the concentrations of oxidant and reductant at the interface must be equal if their diffusion rates are identical. In most reversible polarographic reactions the latter condition is approximated, and Heyrovský and Ilkovič[2] have made this their main assumption in the detailed analyses of the polarographic curves which follow.

When the cathodic current, *i. e.*, the current observed during a reduction, is governed only by the rate of diffusion of the oxidant, it is a function of the difference in concentration between the depleted interface and the body of the solution and can be expressed as follows:

$$I = K([\mathrm{Ox}] - [\mathrm{Ox}]_i) \tag{5}$$

where I is the current and [Ox] the concentration in the body of the solution, while $[\mathrm{Ox}]_i$ is the concentration at the interface. K is the diffusion current constant. When the diffusion current is maximal, $[\mathrm{Ox}]_i$ becomes negligibly small compared to [Ox] and

$$I_d = K[\mathrm{Ox}] \tag{6}$$

Therefore

$$[\mathrm{Ox}]_i = (I_d - I)/K \tag{7}$$

The concentration of the reaction product at the interface $[\mathrm{Red}]_i$ must be proportional to the current I so that

$$[\mathrm{Red}]_i = kI \tag{8}$$

where k is again a diffusion constant.

We can now substitute from equations (7) and (8) into (4) to get

$$E = E_0 - \frac{RT}{nF} \ln \frac{kIK}{I_d - I}$$

or

$$E = E_0 - \frac{RT}{nF} \ln \frac{I}{I_d - I} - K' \tag{9}$$

In the case of the half-wave potential, I is equal to $(I_d - I)$ by definition, so that the logarithmic term drops out:

$$E_{1/2} = E_0 - K' \tag{10}$$

This means that the half-wave potential of the dropping mercury electrode is equal to the normal electrode potential of the reacting system minus some constant. According to Heyrovský and Ilkovič[2] this constant is a function of the diffusion coefficients of the oxidant (D_{Ox}) and reductant (D_{Red}) as follows:

$$K' = \frac{RT}{2nF} \ln \frac{D_{\mathrm{Ox}}}{D_{\mathrm{Red}}} \tag{11}$$

The ratio of the diffusion coefficients is assumed to be close to unity so that K' can usually be neglected.

The crucial test for the correctness of these assumptions and deductions on the one hand, and for the reversibility of the systems on the other hand, is to observe the reverse reactions at the dropping mercury electrode. If K' is negligible, the half-wave potential obtained in the oxidation of the reductant of a reversible oxidation-reduction system should be identical with that obtained in the reduction of the oxidant of the same system.

The first verification of these conclusions was made by Müller and Baumberger[5] who studied reversible organic systems. They found, for example, that within the limits of experimental error the half-wave potential of the reduction of quinone is identical with the half-wave potential of the oxidation of hydroquinone, if the solutions are well buffered. A similar proof for a number of simple inorganic oxidation-reduction systems has been obtained more recently by Heyrovský and Kalousek[6] and by Kalousek.[7]

In practice the reversible reactions are conveniently divided into three groups: the electrodeposition of free metallic ions, the reduction of multivalent metallic ions to a state of lower valency, and the reduction of organic compounds.

Electrodeposition of Free Metallic Ions. This type of reaction is the most used in polarography and takes place according to the following equation:

$$\mathrm{M}^{n+} + n\epsilon \rightleftharpoons \mathrm{M} \tag{12}$$

The free metallic ions are here the oxidant, while the deposited metal atoms which diffuse into the mercury and amalgamate with it are the reductant. We may now test equations (4) and (9) by examining the reduction of monovalent thallium ions.

Experiment 2.—Electrolyze, air-free, between zero and 1.0 volt, a solution of 1.8×10^{-3} *M* thallium sulfate in 0.1 *N* potassium chloride to which one drop of acid fuchsin has been added. The saturated calomel half-cell is reference electrode and is connected to the solution by a potassium chloride bridge. Use the galvanometer shunt at position No. 4. After completing the experiment, determine the resistance of the circuit as suggested in Part II of this series.[3]

[5] *Trans. Electrochem. Soc.*, **71**, 181 (1937).
[6] *Collection Czechoslov. Chem. Commun.*, **11**, 464 (1939).
[7] *Ibid.*, **11**, 592 (1939).

The results are shown in Table 1. If we plot the applied "voltage" V (Column 1) against the corresponding current I (Column 2), we get the "current–voltage" curve a in Figure 3. This is the type of curve that is usually obtained with a recording instrument. For theoretical purposes it is necessary to convert this curve to a "current–potential" curve by subtracting IR from the applied voltage as has been shown before.

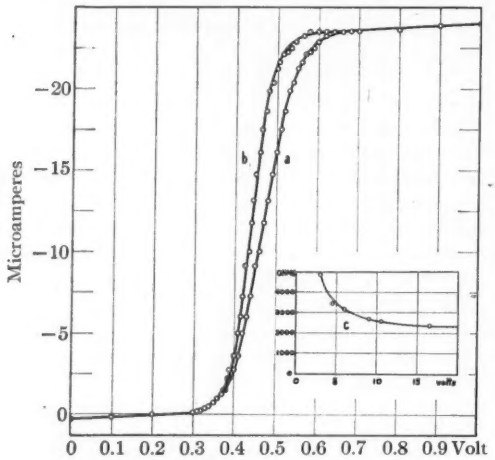


FIGURE 3.—REDUCTION OF THALLIUM IONS
(*a*) Current–voltage curve
(*b*) Current–potential curve
(*c*) Estimation of cell resistance

TABLE 1

V Volt	I × 1.24 × 10^{-6} Amp.	IR Volt	E Volt	$\log \frac{I}{I_d - I}$	V Volt	I × 1.24 × 10^{-6} Amp.	IR Volt	E Volt	$\log \frac{I}{I_d - I}$
0	−0.2	0	..	...	0.48	10.5	0.03	0.45	+0.100
0.10	−0.1	0	0.10	...	0.49	11.8	0.04	0.45	0.225
0.20	0	0	0.20	...	0.50	12.9	0.04	0.46	0.338
0.30	+0.1	0	0.30	−2.273	0.51	14.0	0.04	0.47	0.463
0.31	0.2	0	0.31	−1.969	0.52	14.9	0.05	0.47	0.520
0.32	0.2	0	0.32	−1.969	0.53	15.9	0.05	0.48	0.738
0.33	0.3	0	0.33	−1.791	0.54	16.3	0.05	0.49	0.814
0.34	0.4	0	0.34	−1.664	0.55	17.0	0.05	0.50	0.975
0.35	0.6	0	0.35	−1.481	0.56	17.3	0.05	0.51	1.061
0.36	0.8	0	0.36	−1.353	0.57	17.7	0.05	0.52	1.206
0.37	1.0	0	0.37	−1.252	0.58	17.8	0.05	0.53	1.250
0.38	1.2	0	0.38	−1.167	0.59	18.0	0.06	0.53	1.350
0.39	1.8	0.01	0.38	−0.977	0.60	18.3	0.06	0.54	1.562
0.40	2.2	0.01	0.39	−0.879	0.62	18.6	0.06	0.56	1.967
0.41	2.9	0.01	0.40	−0.740	0.64	18.8	0.06	0.58	...
0.42	4.0	0.01	0.41	−0.570	0.66	18.8	0.06	0.60	...
0.43	4.8	0.01	0.42	−0.466	0.68	18.8	0.06	0.62	...
0.44	5.8	0.02	0.42	−0.351	0.70	18.8	0.06	0.64	...
0.45	7.3	0.02	0.43	−0.198	0.80	18.9	0.06	0.74	...
0.46	8.0	0.02	0.44	−0.131	0.90	19.1	0.06	0.84	...
0.47	9.4	0.03	0.44	0	1.00	19.2	0.06	0.94	...

TABLE 2

Voltage *Volts*	*Current* × 10^{-4} *Amp.*	*Resistance* *Ohms*
3	6.1	4900
4.5	13.1	3440
6.0	18.7	3200
9.0	33	2700
10.5	41	2560
16.5	74	2260

From the data given in Table 2 an approximate value of the resistance of the circuit can be found. The calculated resistance R (Column 3) is plotted against the large applied voltage V (Column 1), and the resulting curve is extrapolated to an infinitely large voltage (see insert, curve c, in Figure 3). Thus we find that the resistance of the cell is about 2200 ohms. To this resistance must be added 250 ohms, which is the resistance of the shunted galvanometer at shunt position No. 4 (see Part II[3]). Using then 2500 ohms as the resistance of the circuit, we can calculate IR (Table 1, Column 3) and subtract this from V to get the electrode potential E (Column 4). This plotted against the current gives us the "current–potential" curve b (Figure 3). If taken at the same temperature such a curve is identical in shape with an electrometric titration curve involving a one-electron change (see Part I,[1] Figures 2 and 3*A*). Yet in the polarographic curve, only the minute quantity of solution present in the interface is titrated, while the body of the solution remains essentially unaltered. The current here corresponds to the quantity of reagent added.

The thallium curve can also be analyzed in another way. For this we need I_d, the diffusion current, which we get from Figure 3. It is 18.8 × 1.24 × 10^{-6} amperes. We can then calculate $\log \frac{I}{I_d - I}$ (Table 2, Column 5). Plotting this quantity against E we should get a straight line with a slope of 0.059 volt. Curve *A* in Figure 4 shows that this is actually the case.

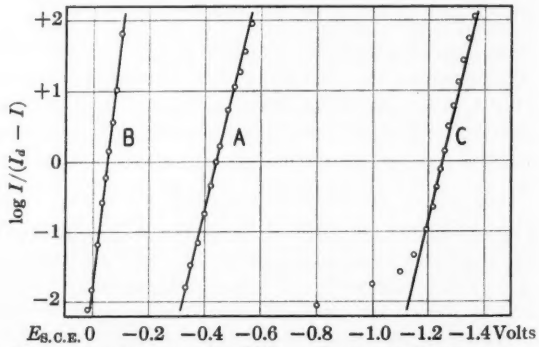


FIGURE 4.—GRAPH OF $\log I/(I_d - I)$ AGAINST POTENTIAL
(*A*) Reduction of thallium ions (from Figure 3)
(*B*) Oxidation of hydroquinone at pH 7 (from Figure 5)
(*C*) Reduction of benzaldehyde at pH 8

In the reduction of a divalent ion, the slope of this curve should be 0.030 volt. Electrolyses of cadmium and lead have confirmed this. In the reduction of a trivalent ion, such as indium, the slope is 0.020 volt.

The backward reaction shown in equation (12), *i. e.*, the anodic dissolution of the metal, gives the same half-wave potentials as the forward reaction if the reaction is reversible. Heyrovský and Kalousek[6] worked with *dilute* amalgam electrodes and found this to be true in the case of copper, lead, cadmium, and zinc.

To this group of reactions should be added with some reservation *the electrodeposition of metals from complex metallic ions*. In analytical polarography much use is

made of the fact that, if a metal is reduced from a complex, the half-wave potential is more negative than that obtained if the metallic ions are free. Heyrovský and Ilkovič[2] assume that the complex between free metallic ions and complex-forming anions is perfectly reversible:

$$M^{n+} + pX^{m-} \rightleftharpoons MX_p^{(pm-n)-} \qquad (13)$$

and can be expressed by an equilibrium (complexity) constant K_c, so that the concentration of free metallic ions, the oxidant in the reaction, is given by:

$$[M^{n+}] = \frac{[MX_p^{(pm-n)-}]}{K_c[X^{m-}]^p} \qquad (14)$$

From this, Heyrovský and Ilkovič calculate that the shift in the half-wave potential is $-(RT/nF) \ln K_c$ if the concentration of the complex former is unity and the diffusion coefficients of the free and complex ions are equal. While this theory has not yet been subjected to critical tests, it serves well as a working hypothesis for finding suitable complexes to separate polarographic potentials which overlap.

The Reduction of Multivalent Ions to a State of Lower Valency. This type of reaction may be represented by

$$M^{n+} + me \rightleftharpoons M^{(n-m)+} \qquad (15)$$

It has been observed polarographically for a long time in the reductions of chromic and cobaltic ions. The cathodic curves have the same form as those due to the electrodeposition of metals, and it seemed logical to assume that they are reversible. Recent tests by Kalousek,[7] however, in which the reverse reactions were studied, showed that this is true only in the case of the cupric–cuprous system, in others only under special conditions.

The Reduction of Organic Compounds. The compounds of reversible organic oxidation-reduction systems are usually weak acids or bases so that in addition to the electrode reaction

$$R + 2e \rightleftharpoons R^{--} \qquad (16)$$

must be added the equilibria

$$R^{--} + H^+ \rightleftharpoons RH^- \text{ and } RH^- + H^+ \rightleftharpoons RH_2 \qquad (17)$$

Since R and RH_2 are the quantities which can be measured directly, it is best to combine these equations and consider R the oxidant and RH_2 the reductant. The electrode potential is then expressed by the well-known equation:

$$E = E_0 - \frac{RT}{2F} \ln \frac{[RH_2]}{[R]} + \frac{RT}{2F} \ln(Ka_1Ka_2 + Ka_1[H^+] + [H^+]^2) \qquad (18)$$

which is written for a two-electron change and in which Ka_1 and Ka_2 are the two dissociation constants of the reductant. Clark and Cohen[8] give a detailed discussion of this and similar equations and their implications. The last term in this equation becomes constant if the pH of the solution is kept constant by a suitable buffer. Under these conditions we have:

$$E = E_0 - \frac{RT}{2F} \ln \frac{[RH_2]}{[R]} + k$$

or

$$E = E'_0 - \frac{RT}{2F} \ln \frac{[RH_2]}{[R]} \qquad (19)$$

If $[RH_2] = [R]$ the last term drops out and $E = E'_0$. It has been shown that this condition exists at the dropping mercury electrode at the half-wave potential in a well buffered solution. This is best demonstrated by a study of the system quinone–hydroquinone, where quinone is the oxidant and hydroquinone the reductant.

Experiment 3.—(*a*) Electrolyze, air-free, a solution of one cc. 0.02 *M* quinone and 9 cc. McIlvaine buffer of pH 7, between +0.5 and −0.5 volt, using a saturated calomel electrode as reference electrode and a saturated *potassium nitrate* bridge as liquid junction. Add some platinized asbestos and free the solution from atmospheric oxygen by means of nitrogen gas. Thus all of the quinone remains oxidized. Use "anodic and cathodic polarization"[3] since the half-wave potential of this curve is near that of the calomel half-cell.

(*b*) After curve *a* has been obtained, pass through the solution some hydrogen gas which in the presence of platinized asbestos will reduce the quinone to hydroquinone. During this chemical reduction observe the diffusion current of the quinone at a constant voltage of −0.5 volt. When the current has dropped to almost half its former value, stop the flow of hydrogen and blow out the system with some nitrogen gas. The solution has now been changed from one containing only oxidant (quinone) to one which contains also a measurable amount of reductant (hydroquinone). Since the reducing agent was gaseous hydrogen the total concentration of oxidant plus reductant has not been changed. Repeat the above electrolysis under these new conditions.

(*c*) Reduce the solution further with more hydrogen gas until the diffusion current of quinone at an applied voltage of −0.5 volt has disappeared. All the quinone has now been changed into hydroquinone and the solution is now one that contains pure reductant. Repeat the electrolysis under these conditions.

(*d*) Finally measure the resistance of the circuit as in Experiment 2.

The results of this experiment are shown as "current–potential" curves in Figure 5. Notice that all three curves have half-wave potentials which are identical within the experimental error. The wave-heights of the quinone and hydroquinone curves are in a ratio of 15.3 to 14.1. If none of the quinone has been destroyed during the reducing process this ratio must express the ratio of the square roots of the diffusion coefficients of quinone and hydroquinone.[4] Since this is not exactly unity, the half-wave potentials of the cathodic and anodic curves should not be perfectly identical, a conclusion that, unfortunately, cannot be checked because of the inaccuracy of our measurements. For example, if we analyze the curve *c*, which is due to the oxidation of hydroquinone, by plotting $\log \frac{I}{I_d - I}$ against E we find that the observed points fit the theoretical curve with a slope of 0.030 volt (Figure 4, curve *B*).

[8] *Public Health Reports*, **38**, 666 (1923).

It may be noticed that the currents obtained in the oxidation of hydroquinone suddenly drop to very small values when critical potentials are reached. This is not the same phenomenon as the well-known maxima.[4] Instead it represents the change from an electrode which indicates the presence and ratio of foreign oxi-

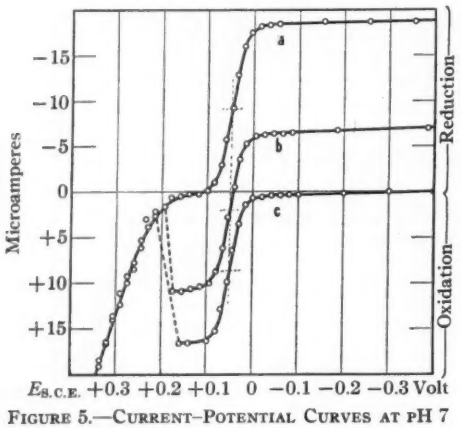


FIGURE 5.—CURRENT–POTENTIAL CURVES AT pH 7
(*a*) Quinone
(*b*) Quinone, partly reduced by platinized asbestos and hydrogen gas
(*c*) Quinone, fully reduced by platinized asbestos and hydrogen gas

dants and reductants at its surface to one which actively participates in the reaction by sending its ions into solution. In the present case the indifferent mercury electrode, which showed the ratio of quinone to hydroquinone, changed to an active electrode, producing mercurous ions which formed a complex with the phosphate ions present. More cannot be said here about this phenomenon. Studies concerning it are still in progress in this laboratory.

Quinhydrone is a compound which dissociates in solution into equal parts of quinone and hydroquinone. A polarogram of quinhydrone in a buffered solution, therefore, shows a single wave, half of which is anodic while the other half is cathodic. At the midpoint of this curve practically no current flows. The polarographic half-wave potential coincides in this particular case with the potentiometrically determined potential of any indicator electrode immersed in the same solution.

If these reversible organic reductions proceed in such a way that the two electrons [equation (16)] are added separately at different potentials, with the formation of intermediate radicals (semiquinones), or if the reductions are carried out in unbuffered solutions, complicated polarographic curves result which have been analyzed in detail but cannot be described here.

IRREVERSIBLE REACTIONS

Not much space can be devoted to the large number of irreversible reductions that have been studied polarographically. In some of these the current increases abruptly (*e. g.*, in the reduction of nitrate ions in the presence of lanthanum), in others the wave loses its symmetry around the midpoint. Some seem perfectly reversible, judging from the shape of the curve, but the reaction product is not known with certainty and cannot be used for a study of the backward reaction. Studies of these reactions are therefore largely empirical, and it is questionable that the half-wave potential in these cases is constant at different concentrations and drop-times, because the rates of reaction play a major part in determining the potentials. The following may serve as a typical experiment.

Experiment 4.—Electrolyze, air-free, one cc. of 0.02 *M* benzaldehyde and 9 cc. McIlvaine buffer of pH 8 between +0.8 and 2.0 volts, using a saturated calomel half-cell as reference electrode and a potassium nitrate bridge as liquid junction. Use position No. 4 of the galvanometer shunt. Determine the resistance of the circuit at the end of the experiment.

The resulting "current–potential" curve is not reproduced here. Instead, we have plotted $\log I/(I_d - I)$ against E in Figure 4, curve *C*. As may be seen, no straight line is obtained but the end of the curve approaches the theoretical curve with a slope of 0.059 volt, indicating a reaction involving the transfer of one electron per molecule. This is a typical irreversible reaction because it is impossible to find an end-product which would give the same curve anodically. It makes little difference if one uses the half-wave potential or any of the empirical designations of potential to characterize these reductions, as long as one remains consistent throughout.

Many of these reductions show a dependence on the pH, suggesting partial reversibility in the process. A few detailed investigations of such curves have been made which seem to indicate that the polarographic curve shows the reversible step in a reaction which is on the whole irreversible.

Only one similarly irreversible anodic reaction is known so far. It is the anodic oxidation of ascorbic acid.

Finally should be mentioned reactions which involve the oxidation of the mercury electrode itself to mercurous ions. An example has been given in Experiment 3*c*. Phosphate ions or other ions which react with mercurous ions to form a precipitate or complex will depolarize the electrode. Depending on their concentration, anodic waves of varying heights and with characteristic potentials for each depolarizer are thus obtained. The curves are not the usual S-shape and the half-wave potentials are not independent of concentration.

New Data for Placement Procedures

ANDREW H. MACPHAIL and LAURENCE S. FOSTER *Brown University, Providence, Rhode Island*

IN 1939 we described the technic used at Brown University as an aid in the proper placement of students in beginning chemistry courses,[1] and pointed out that better placement resulted from the use of multiple correlations involving the scores on various aptitude criteria. In that report, the Iowa Chemistry Training Test, the Mathematical Section of the Sones-Harry High-School Achievement Test, and the Brown University Psychological Examination were found to give the highest multiple correlations with the performance of students in the general college chemistry course. Recently, Brown has made some changes in the content of the battery of tests given to entering students just prior to the opening of college. The purpose of this note is to present some correlations, based on data from the new tests. In Table 1 are presented the three-variable multiple correlations, *R*'s, of the 1940 study. The following conclusions have been drawn: The standing of the students in their high-school graduating classes, when properly weighted and combined with scores on the Iowa Chemistry Training Test, gives the highest predictive combination, but the scores on the Iowa Chemistry Training Test, combined with either the scores on the Coöperative General Mathematics Test or the Q scores on the Psychological Examination of the American Council on Education, are almost as good. The L scores on the American Council Psychological Examination have no significant predictive value for general college chemistry.

TABLE 1

R'S TO PREDICT GENERAL CHEMISTRY GRADES, 1940 STUDY

R	*Variables*	(*N* = 70)
0.57	General chemistry grades High-School Rank* Iowa Chemistry Training Test†	
0.52	General chemistry grades Iowa Chemistry Training Test† Coöperative General Mathematics Test‡	
0.52	General chemistry grades Iowa Chemistry Training Test† Q Score (A.C.E.)§	
0.41	General chemistry grades Iowa Chemistry Training Test† L Score (A.C.E.)‖	

* High-school rank on a sigma scale.

† Published by The Bureau of Educational Research and Service, Extension Division, The State University of Iowa, Iowa City, Iowa, Series C.T.-1, Revised B.

‡ Published by Coöperative Test Service, 15 Amsterdam Avenue, New York City.

§ American Council on Education Psychological Examination, published by the American Council on Education, 744 Jackson Place, Washington, D. C.

‖ Same as §.

Obtained grades have been correlated with predicted grades with satisfactory results, as indicated by the fact that one regression equation used for predicting represented an *R* value of 0.57 and the *r* for predicted and obtained grades for 59 students was 0.60. In another case involving 80 students, the equation used for predicting represented an *R* value of 0.52 and the correlation between predicted and obtained grades was 0.66.

In addition to the three-variable data reported the following regression equation ($R = 0.61$) was computed for four variables:

General Chemistry Grade = 0.16 Iowa Score + 0.33 High-School Rank on a sigma scale + 0.27 Coöperative General Mathematics Score + 23

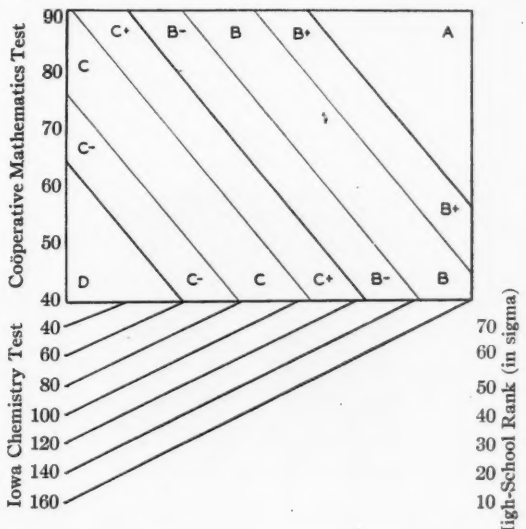
For the same 80 students just cited, grades predicted by means of this formula correlated 0.76 with obtained grades.

In the 1939 article we presented two examples of three-variable charts based on regression equations. Here we show a chart based on the above four-variable equation. Through its use predictions can be made without actually solving the equation for each student. For example, a student with a high-school rank of 50, an Iowa score of 160, and a mathematics score of 75 would have a predicted chemistry grade of "middle" B. Solving the equation gives 85. This set of values is read on the chart as follows:

Start with a high-school rank of 50 on the scale at the lower right of the chart, then read horizontally to the left as far as the diagonal line marked 160 on the Iowa scale at the lower left of the chart; from that point read straight up to the point directly opposite the value of 75 on the mathematics scale at the upper left of the chart. The point thus reached falls in the "middle" B zone.

CHART FOR PREDICTING CHEMISTRY 3 GRADE

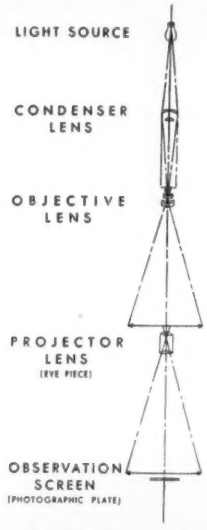
From Scores on Coöperative Mathematics Test and Iowa Chemistry Training Test and High-School Rank (in sigma).



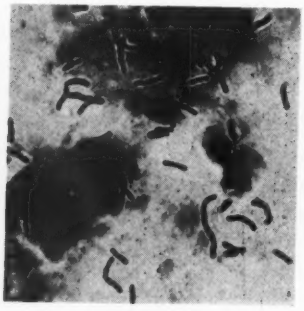
[1] MACPHAIL AND FOSTER, J. CHEM. EDUC., **16**, 270 (1939).

An Ordinary Microscope
Focuses light with glass lenses

Courtesy of the Bausch and Lomb Optical Company



Courtesy of the RCA Research Laboratories



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The Electron

THE scientist today stands at the threshold of a vast new world of chemistry, opened up by the electron microscope.

In principle the electron microscope focuses *electrons* with *magnetic* lenses, just as an ordinary microscope focuses *light* with *glass* lenses. The shorter the wave length, the greater the resolving power. The wave lengths of photons, or visible light, are from 4000 to 8000 A.; electrons have a wave length of about 0.01 A.

Although cathode-ray images were obtained as early as 1876 (Goldstein), it was not until 1926 that the lens properties of magnetic and electric fields were demonstrated (Busch). This was shortly before Davisson and Germer[1] showed that electrons behaved like light waves. Pioneers followed in quick succession: Rupp (1928), Zworykin (1929), Davisson of the Bell Telephone Laboratories (1931), and Brueche and his collaborators in Berlin (1932), using electrostatic lenses. The first compound magnetic lens microscopes, progenitors of the 1941 streamlined RCA model, were developed in Germany by Knoll and Ruska (1932); and at the University of Brussels by Marton, who was also the first to use his instrument for biological studies (1934).

Several years later at the University of Toronto Burton, Hillier, and Prebus constructed a similar instrument. In one study with this machine colloidal carbon was magnified 102,000 diameters, revealing it to be spheroidal, averaging 28 millimicrons in diameter—about half the value indicated by ultramicroscopic counting methods.

Interested in electron optics for many years, the RCA laboratories at Camden, New Jersey, supported the development of a research model of the electron microscope by L. Marton under Associate Director V. K. Zworykin. Recently, a streamlined model suitable for routine or research laboratories has been developed there by J. Hillier. This instrument is now being made for sale at $9500. The first purchaser was the American Cyanamid Company, who, in six weeks' time, obtained interesting results of fundamental importance.

In the electron microscope, electrons are generated by a tungsten filament, accelerated to 30,000–60,000 volts by a strong electric field, and then magnetically focused upon the object to be examined. This corresponds to gathering light with the condenser lens of a microscope. The object, such as a typhus bacillus, is mounted in a nitrocellulose film a millionth of an inch thick, supported on a fine wire cloth. Although the entire apparatus must be evacuated to 10^{-4} mm., pictures may be taken in rapid succession, since the RCA instrument is equipped with air-lock chambers which admit air to only a small section of the apparatus when changing samples. The electrons pass through the sample and are guided by the magnetic field of the "objective" to a fluorescent screen, where an image of the object, magnified one hundred-fold, is produced. This image is then further magnified by a projection coil, similar to that used in television, to produce a second image on a fluorescent screen or photographic plate with magnifications up to 20,000. The picture recorded by these electrons has been named an *electron micrograph* as distinguished from a *photograph* obtained with photons. The electron micrograph is usually so clear that it may

[1] GERMER, "Optical experiments with electrons, Parts I and II," J. CHEM. EDUC., **5**, 1041, 1255 (1928).

Microscope

be photographically enlarged to as much as 100,000 diameters beyond which there is no improvement in definition.

Conservatively speaking, a sample which is enlarged 100,000 diameters under the electron microscope would be as clearly resolved as a 1500-diameter magnification by an ordinary optical microscope. More simply, the ordinary microscope can detect particles some 1500 A. in diameter, but the electron microscope goes down to 30 A. Since atoms are only one-tenth this size, chemists can nearly—but unfortunately not quite—peer into a world which first existed in the minds of Democritus, Lucretius, and Dalton. Giant molecules can even now be photographed, but there is some distance yet to go before individual atoms will be revealed.

During recent months the RCA Laboratories, in collaboration with Dr. Stuart Mudd of the University of Pennsylvania, chairman of a committee of the National Research Council on the electron microscope, have examined the structure of germ cells which appear as mere specks in an ordinary microscope. They have found, for example, that streptococcus germs are bound in chains by rigid and continuous outer membranes, and have examined the internal structure of whooping cough germs and the structure of the flagellae of typhoid germs. Dr. H. Morton and Thomas F. Anderson have discovered that tellurite salts within diphtheria bacilli are reduced to crystals of tellurium, the crystals perforating the cell walls in some cases. Dr. Anderson also took the electron micrograph shown here of the tobacco mosaic virus prepared by Dr. W. M. Stanley of the Rockefeller Institute.

In this picture note the interesting spiral internal structure of the bacterium. Adhering to its tip may be seen the rod-shaped particles of the tobocco mosaic virus which, being crystallizable, has all the properties of a pure chemical substance. Neither these nor the small specks of normal rabbit serum can be seen under an ordinary microscope.

Micrographs were also taken showing the molecular structure of soap crystals. Many industrial companies are examining their products under the RCA electron microscope. Rouge at 15,000 diameters exhibits jagged edges; carbon particles in a gas flame and crystals in cigar smoke are easily identified by their distinctive shapes; synthetic fibers and plastics reveal the secrets of their molecular structure to the electron microscope.

At the Kodak Research Laboratories the development of the photographic image is being studied. Under such high magnification, the so-called "grain" of silver turns out to be more like a clump of seaweed than a solid speck. Such studies will undoubtedly lead to the production of better fine-grain films.

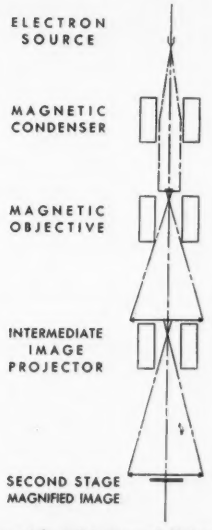
In Germany, Ruska at the Siemens and Halske A. G., and Brueche in Berlin describe: studies of mine dusts for health protection; micrographs showing that the forces holding adsorbed red gold sols to tobacco mosaic virus below pH 4.5 are so strong that the gold cannot be aggregated to the blue form, as it normally is upon the addition of sodium chloride; micrographs of individual molecules of hemocyanin from the blood of mollusks and of edestin particles from vegetable oils.

The new field of electron microscopy, realm of molecular studies, lies unexplored.

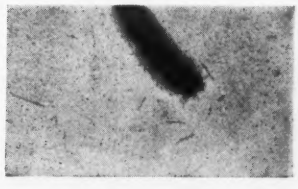
We are indebted to Dr. Thomas F. Anderson, RCA Electron Microscope Fellow of the National Research Council for 1940 to 1941, and to Dr. W. M. Stanley of the Rockefeller Institute, for supplying the accompanying micrograph. —H. N. Alyea

The Electron Microscope
Focuses electrons with magnetic lenses

Courtesy of the RCA Research Laboratories



Courtesy of the RCA Research Laboratories



Bacterium under Electron Microscope, Reacting with Tobacco Mosaic Virus. Magnification—1:13,800

The Application of Organic Reagents to Inorganic Analysis[1]

J. A. SOUTHERN

Furman University, Greenville, South Carolina

WITHIN the past two decades rapid strides have been made in the application of organic compounds as analytical reagents, both in qualitative and quantitative analysis. To be sure, certain organic reagents were used prior to this period of rapid development but the number was small. During the same time micro and semimicro methods of analysis have been adapted to many methods of macro analysis, both qualitative and quantitative. While the use of organic reagents has not been responsible for the shift to the micro and semimicro methods, certainly their application has played a large part in this transformation.

The question is often asked: Why has the analytical chemist waited so long to use such an important tool? Perhaps he was content to use inorganic reagents for inorganic reactions and leave the organic compounds completely to the organic chemist. The organic chemist, on the other hand, was not interested in seeking analytical application for the many organic compounds at his disposal or the new ones which he made. The two did not get together, and progress in the field was retarded. Hundreds of organic compounds have been available to the analyst without any effort on his part to seek analytical application for them. One chemist makes the statement that he had dipicrylamine in his laboratory for twenty-five years without once thinking it might have analytical value.[2] This compound is now a well-known reagent for the detection of potassium.[2]

Among the earlier applications of organic reagents are the Griess reaction for nitrous acid[3] and the cobalt reagent, α-nitroso-β-naphthol, described by Ilinsky and Knorre.[4] The use of dimethylglyoxime as a precipitant for nickel[5] really marked the beginning of progress in this field. The contribution of Alfred Werner concerning valence and coördination compounds[6] had an important bearing on the use of organic reagents. The advent of "spot test" analysis some twenty years ago[7] became the impetus also for a vast amount of subsequent research.

What are the advantages of organic compounds over the inorganic reagents generally used in qualitative and quantitative analysis?

In the first place many of these compounds are colored and produce highly colored compounds with the metal ions, which are themselves colorless. In many cases there is a change in hue. This factor is of qualitative analytical value. As an example we might cite the case of bismuth. If bismuth hydroxide is precipitated with ammonium hydroxide, with only a trace of bismuth present, the water-white precipitate is almost invisible in aqueous suspension. However, with a few drops of a cinchonine-KI solution, which is colorless, an orange-red precipitate is produced.[8] An even more vivid illustration is furnished with magnesium. Potassium hydroxide precipitates the semi-transparent, gelatinous magnesium hydroxide. With only a trace of magnesium it is impossible to see the precipitate, but if the same precipitate is formed in the presence of *p*-nitrobenzeneazo-α-naphthol, it takes on a blue color and becomes visible.[9] By this procedure one part of magnesium in 4,500,000 parts of solution may be detected if the suspension is extracted by shaking with chloroform, and the extract concentrated. The majority of the tests in qualitative analysis in which organic reagents are employed depend upon a change in color of the solution or the formation of a highly colored precipitate.

Another factor which makes the organic compounds of the metals applicable, both qualitatively and quantitatively, is their low solubility in aqueous solutions and, in many cases, high solubility in organic solvents. This has its advantage in effecting separations of metals preceding their final detection and determination. Also the fact that many of these compounds are soluble in organic solvents makes colorimetric determinations possible.

A third factor facilitating the use of organic compounds as qualitative reagents is their high sensitivity, largely dependent on their great coloring power and insolubility. The low metal content of the organometallic compound also adds greatly to the sensitivity. This makes possible a large amount of precipitate with a small concentration of metal, which means a very low "chemical factor." For example, aluminum forms a compound with morin,[10] which has a chemical factor of 0.0284. Further, note the metal content of some of the 8-hydroxyquinoline-metal compounds as compared with the same metal in inorganic compounds as they are usually determined.

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[1] Presented before the Division of Chemical Education at the one-hundredth meeting of the A. C. S., Detroit, Michigan, September 12, 1940.

[2] DUBSKY, *Mikrochemie*, **23**, 24 (1937); WINKEL AND MAAS, *Z. angew. Chem.*, **49**, 827 (1936).

[3] GRIESS, *Ber.*, **12**, 427 (1879).

[4] ILINSKY AND KNORRE, *Ber.*, **18**, 699 (1885).

[5] TSCHUGAEFF, *Ber.*, **38**, 2520 (1905).

[6] WERNER, *Z. anorg. allgem. Chem.*, **3**, 267 (1895).

[7] FEIGL AND STERN, *Z. anal. Chem.*, **60**, 1 (1921).

[8] LEGER, *Z. anal. Chem.*, **28**, 347 (1889).

[9] FEIGL, "Qualitative Analyse mit Hilfe von Tupfel-Reaktionen," 3rd ed., Akademische Verlagsgesellschaft, Leipzig, 1938, p. 6.

[10] SCHANTL, *Mikrochemie*, **2**, 174 (1924).

Organo-metallic compound	*Chemical factor*	*Usual weighed form*	*Chemical factor*
$Al(C_9H_6NO)_3$	0.0587	Al_2O_3	0.5291
$Cd(C_9H_6NO)_2$	0.2792	$CdSO_4$	0.5392
$Cu(C_9H_6NO)_2$	0.1808	CuO	0.7985
$Mg(C_9H_6NO)_2 \cdot 2H_2O$	0.0698	$Mg_2P_2O_7$	0.2184
$Bi(C_9H_6NO)_3 \cdot H_2O$	0.3171	Bi_2O_3	0.8965
$Zn(C_9H_6NO)_2 \cdot 1^1/_2H_2O$	0.1718	ZnS	0.6710

The specific action of organic reagents is another property which makes them adaptable to analytical work. While at present there are only a very few cases of absolute specific action, in many situations the conditions of the test and the nature of the solution may be so altered as to eliminate the effect of interfering ions. The use of dimethylamino-benzylidine-rhodanine in the detection of silver affords a good example.[11] While this compound reacts with silver, mercury, copper, gold, palladium, and platinum, it is possible, by masking the solution properly, to detect silver in the presence of all other metals.[12, 13]

Of interest are those organic compounds which have within their molecules certain atomic groupings more or less specific for certain metal and non-metal ions. The ideal situation would be that of absolute specificity for every metal; then qualitative analysis would be just a succession of final tests for the several ions. But at the present time the situation is far from that ideal. It is felt that the solution to the problem lies in the makeup of the metal ion rather than in the organic compounds. When more fundamental knowledge is at hand concerning the reason for differences in the properties of the metals and their compounds, the chemist may be able to predict what type of atomic grouping in the organic compound will be suited for use with the individual ions. At present, research on organic compounds as specific reagents for the metal ions cannot be based altogether on any definite principles, but must be largely empirical.

There are, however, a few instances of certain groups which under proper conditions are specific in their action toward certain metal ions. We have already mentioned dimethylglyoxime,[5] first employed by Tschugaeff for the identification and subsequently for the determination of nickel. Other α-dioximes are capable of forming colored salts with nickel, which are for the most part red. Among them are α-furildioxime,[14] α-benzildioxime,[15] and cyclohexanedione dioxime.[16]

To mention some other compounds which are more or less specific for certain metal ions, α-benzoin oxime[17] and salicylaldoxime[18] are used for the detection of copper, α-α'-dipyridyl and α-α'-phenanthroline for ferrous iron,[19] α-nitroso-β-naphthol for ferrous and cobaltous ions,[4] and the hydroxyanthraquinones form very stable salts[20] with the trivalent metals such as aluminum, iron, and chromium.

The stability of compounds formed by the organic reagents and the metal ion is another factor favoring their use in analytical work. Most of the reactions between a metal ion and an organic compound result in salt formation due to the replacement of acidic hydrogen by the metal and the union of the metal at the same time to another part of the organic molecule by a covalent linkage. In this manner a ring structure, composed of five or six members, results, which according to the Baeyer strain theory should produce a very stable compound. Some very striking illustrations of the stability of these compounds are afforded by the aluminum salts of the 1,3-diketones, which may be volatilized without decomposition,[21] and the copper salt of one of the phthalocyanines, so stable to heat that it undergoes no decomposition even when distilled in a vacuum above 500°C.[22]

Most of the reactions between a metal ion and an organic reagent result in salt formation, through replacement of an active hydrogen, and ring-closing by a covalent linkage. This gives what is known as the chelate ring. According to Werner the large number of complex compounds may be divided, on the basis of their origin and structure, into two groups: the "addition" and "penetration" compounds.[23] A third group of complex compounds is designated by Ley as "inner complex" compounds.[24] The members of this group form chelate rings, and are by far the most important among organic reagents. They are formed as previously indicated. Therefore it is necessary for a molecule to possess salt-forming properties at one place and coördinating properties at another. Aminoacetic acid displays this type of structure, and its copper salt shows in many respects the behavior of a complex compound. It cannot add ammonia, but exhibits a deep blue color, and possesses a very low electrical conductivity in aqueous solutions.[25] The copper has not only replaced the hydrogen in the acid group but is also bound to the amino group. Iminodiacetic acid produces a similar salt with the cupric ion.[26] These salts are of the inner complex type and possess ring structures. The most stable systems are those which have five or six members in the ring. Alpha-aminoacetic acid forms a five-membered ring, the beta-amino acids form six-membered rings, while the gamma and delta-amino acids do not form inner complex salts with the metals. The possibility of formation of inner complex salts depends, therefore, on the spatial relationship of the salt-forming and coördinating groups.

These inner complex salts are for the most part non-electrolytes, and since the binding forces of the metal

[11] FEIGL, *Z. anal. Chem.*, **74**, 380 (1929).
[12] HELLER AND KRUMHOLZ, *Mikrochemie*, **7**, 214 (1929).
[13] FEIGL, KRUMHOLZ, AND RAJMANN, *Z. anal. Chem.*, **9**, 295 (1931).
[14] SOULE, *J. Am. Chem. Soc.*, **47**, 981 (1925).
[15] ATACK, *Analyst*, **38**, 316 (1913).
[16] WALLACH, *Ann.*, **437**, 148 (1924).
[17] FEIGL, SICHER, AND SINGER, *Ber.*, **58**, 2394 (1925).
[18] EPHRAIM, *Ber.*, **63**, 1928 (1930).
[19] BLAU, *Monatsh.*, **19**, 647 (1898).
[20] MOEHLAU, *Ber.*, **46**, 443 (1913).
[21] FEIGL, "Qualitative Analyse," *op. cit.*, p. 33.
[22] ROBERTSON, LINSTEAD, AND DENT, *Nature*, **135**, 506 (1935).
[23] WERNER AND PFEIFFER, "Neure Auschauungen auf dem Anorganisch Chemie," 5th ed., Vieweg, Braunschweig, **1923**, p. 30.
[24] LEY, *Elektrochemie*, **10**, 954 (1904).
[25] FEIGL, "Qualitative Analyse," *op. cit.*, p. 20.
[26] DUBSKY AND SPRITZMANN, *J. prakt. Chem.*, **96**, 113 (1917).

are saturated by the same molecule it would be expected that there would be little or no dissociation.

The atoms most favorable for the formation of the coördinating link with metals are the oxygen of the carbonyl and hydroxyl groups, the nitrogen of the amino, nitro, nitroso, imino, and oxime groups and the sulfur of the thiocarbonyl group, while the groups which are salt-forming are the sulfonic, carboxyl, hydroxyl, sulfhydryl, oxime, and imine.

The nature of the metal itself must also be considered. For example, the copper salt of aminoacetic acid, mentioned above, is a typical inner complex compound, while the corresponding cadmium and zinc salts are not considered as such, because of their high electrical conductivity. However, these latter metals form ammonia compounds analogous to those of copper.

In addition to inner complex compound formation, many organic reagents react in other ways, such as straight double decomposition, oxidation-reduction, catalytically.

Experimentation in the use of organic reagents has gone beyond the empirical stage. In place of trial and error, certain principles of reactivity have become evident, so that today predictions may be made as to the reactivity of an organic compound with metal ions. Nevertheless, empirical research will yet have to continue, as there are many exceptions and unusual reactions.

Summarizing the principles which must be considered in selecting an organic compound as a reagent for inorganic analysis:

1. Simultaneous presence of atomic groupings which are capable of salt and complex formation.

2. Possibility of the formation of five- or six-membered rings. This is the case with all compounds which have inner complex salt-forming properties.

3. Influence of molecular structure and size on the solubility of the reagent and the organo-metallic compound. Water solubility of the reagent is desirable, but seldom found. On the other hand, the final product should be insoluble in aqueous solutions, while solubility in organic solvents is desirable.

4. Influence of the solution, the precipitating media, and the effect of "masking" agents.

5. Influence of substituent groups and molecular weight on sensitivity and color change. Many reagents have been improved by "tacking on" groups which increase the molecular weight or which have coloring properties.

The application of these principles in the study of the large number of organic compounds now available will aid in the selection of better reagents.

CHEMICAL MICROSCOPY AND OTHER SUMMER COURSES AT CORNELL

COURSES in inorganic, organic, analytical, and physical chemistry will be offered at Cornell University in a six weeks' Summer Session beginning July 7.

Instruction in chemical microscopy will also be given, covering micrometry and particle-size determination, optical studies of crystals and their behavior, lens systems, illumination, ultramicroscopy, photomicrography, and studies of textile and paper fibers. In addition, a course in microscopical qualitative inorganic analysis will be offered. By correspondence in advance, persons not desiring university credit may arrange to cover, in a shorter term, those portions of the field most suited to their needs. Inquiries should be addressed to C. W. Mason, Department of Chemistry, Cornell University, Ithaca, New York.

CONCERNING THE SELECTIVE SERVICE ACT

THE general session at the recent St. Louis meeting of the American Chemical Society included a discussion of the relation of the chemical profession to selective service. The speakers, Dr. Charles L. Parsons, Secretary of the Society, and Major Joseph S. Battley, Chief of the Occupational Deferment Division of the Selective Service System, discussed the application of the Act as it concerns chemists and students of chemistry. It was brought out clearly and most emphatically that the need for trained chemists and chemical engineers is so great as to make it inadvisable for any chemist or student of chemistry to leave his work or his studies to enlist in the armed forces. While there can be no general provisions for group deferment, it is clearly the policy and intention of the Selective Service System to make sure that men who are necessary for the operation of necessary industries, *or who are in training for such positions*, shall not be drafted for military service. Since it is the intention to interpret the implied qualifications in the most liberal sense, this statement should go far toward relieving the anxieties of many students who wonder what the immediate future has in store for them. These were advised that the most helpful and patriotic course for them to follow is to continue their present training and, when the time comes, to apply to their local boards for occupational deferment, since their technical services will be their most valuable contribution to national defense. If local boards refuse such deferment, they are advised to appeal to the higher authorities. While every case of deferment must be acted upon individually, the very large percentage of cases which have been allowed shows that local boards have, in general, been aware of the essential nature of technically trained men, especially chemists. No chemist need feel himself in any sense a "slacker" because he chooses to serve in the capacity for which he is best suited.

Industries and educational institutions, on the other hand, were urged to make every effort to support the claims of chemists and students of chemistry for occupational deferment under the Act, to the end that the industrial machinery of the country—which is so essential in the present emergency—shall not be dislocated or impeded by the withdrawal of necessary skilled and trained workers.

Demonstrations vs. Chemistry Laboratory for Freshman Engineers

SAUL B. ARENSON *University of Cincinnati, Cincinnati, Ohio*

AT THE University of Cincinnati there are five elementary courses in general chemistry given to students in: (*a*) liberal arts; (*b*) evening college; (*c*) business administration; (*d*) chemical engineering, and (*e*) all other fields of engineering. The subject of this paper is the course (*e*) given to freshman non-chemical engineers, and has nothing to do with any of the others.

Up to three years ago, that course was a conventional orthodox course, consisting of four to five lectures, a three-hour laboratory period and a one-hour quiz section per week. At present the lecture and quiz section hours are still unchanged but the three-hour laboratory period has been changed into one-hour demonstrations late in the afternoon on two days a week.

These demonstrations are not the simple ones performed by the teacher during the regular class hour—those are still part of the lecture routine. Nor are they necessarily the same experiments which the student would perform in the laboratory. The easiest way to explain them is to give a few examples.

An experiment found in practically every laboratory manual involves heating $KClO_3$ and MnO_2, and testing the O_2 thus made. That is practically a repetition of what students have seen their lecturer do, during lecture hour. But one of our experiments on O_2 to the engineers consists in a demonstration—usually spread out over two or three periods—showing the use of O_2 in the determination of the calorific value of a coal sample. During that demonstration everything is done except the firing of the sample. The bomb is loaded, the apparatus assembled and explained, and typical time–temperature data are given. The students, having inspected the apparatus, having looked through the telescope at the mercury level in the Beckmann thermometer, then draw a time–temperature ignition curve during the demonstration period. Finally, they calculate the calorific value of the coal in B.t.u./lb. and cal./g., making, of course, all necessary corrections. Not only that, but they are given data on another coal sample and are required to find out which sample gave more B.t.u./dollar.

Likewise the calorific value of a gas is demonstrated. These experiments should give to non-chemical engineers a better appreciation of the work of the chemist and chemical engineer.

The usual experiment performed by students on glass bending involves making a wash bottle and getting it approved. For our demonstration on glass working, a graduate student or faculty member who is an expert glass manipulator demonstrates the simple things about glass bending. Then in the rest of the period he shows how to make T-tubes, how to put side arms on flasks, how to work pyrex glass, why hard glass cannot be sealed on to soft glass, how metal wires are inserted in glass, etc.

"So you expect the student to be able to duplicate that expertness, having seen it done?" asked someone during a discussion of this plan. In the first place, the students seeing this demonstration are never going to do any glass bending unless these non-chemical engineers get a job making neon lamps—which is quite unlikely. In the second place, even if they had performed the simple experiments themselves, they couldn't classify themselves as experts. What these students are learning, among other things, is an appreciation of what has to be done to glass by the glass worker—what can be done and what cannot. Certainly those students who are going on with chemistry need the experience of glass bending, preliminary to their courses in organic and physical chemistry. But why do these non-chemical engineering freshmen need to burn their fingers making glass bends?

Some more examples: To illustrate specific gravity, the student is shown various pieces of apparatus, ranging from simple apparatus to that used in physical chemistry research. He gets acquainted with specific gravity spindles, hydrometers, pycnometers, Westphal balances, and other instruments, and recognizes their accuracy and usefulness.

To emphasize viscosity, various viscosimeters, from a pipet on up, are brought into the demonstration room. Samples of oil are run on a "Saybolt" under varying conditions of temperature. That certainly should emphasize the principles of viscosity needed by an engineer.

Many of the experiments are quantitative in nature and most of them, with preliminary preparation by the instructor, can be performed in twenty minutes, leaving a half hour for discussion, calculating results, and evaluating the data.

To get the students to appreciate the work of the analytical chemist, and to teach them the principles of normal solutions at the same time, the following are demonstrated:

(*a*) Per cent NaOH in lye
(*b*) Per cent Na_2CO_3 in soda ash (two ways)
(*c*) Per cent Fe in iron ore
(*d*) Per cent I_2 in tincture of iodine
(*e*) Per cent Cu in ore (an indirect determination)
(*f*) Per cent N in a fertilizer (Kjeldahl)

To emphasize the principle of fractional precipitation, a titration is run determining the per cent of NaCl by the Mohr method.

Not only are some of the nicest experiments of quantitative analysis run as demonstrations, but the cream

of the physical chemistry experiments is likewise stolen. Usually the experiments are first performed with relatively simple apparatus, such as freshmen themselves could handle. The errors involved in the use of the crude apparatus are discussed, then the real physical chemistry apparatus is introduced to show the refinements. The principle is put across by the simple experiment, so that the students will not lose sight of the fundamentals involved because of the multitude of complicating details in the elaborate apparatus.

An experiment in photography can be performed, in a semidarkened room, doing everything except the development of panchromatic film. Intensifying, reduction, making of blue prints—all of those are processes of interest to the average freshman engineer.

There are many reasons for this sort of change from laboratory to demonstrations. Many teachers believe that, per hour of teaching, laboratory instruction is a very inefficient method. No matter how you try to influence students to ask questions of the laboratory assistants, they always get a great deal of their information from their neighbors. In our demonstrations, the faculty lecturers answer the many questions. The trouble of checking in and out of laboratory is eliminated. The lessened number of students taking laboratory avoids congestion at the stockroom window. Even the saving of chemicals is no small item. But the main purpose, let me repeat, is better instruction in the way that it will do this type of student the most good.

101st MEETING OF THE AMERICAN CHEMICAL SOCIETY

DIVISION OF CHEMICAL EDUCATION

St. Louis, April 7–11, 1941

MEETING OF THE EXECUTIVE COMMITTEE

AT A meeting held at 5:00 P.M. Tuesday, April 8, 1941, the following members were present: R. D. Reed, Chairman, N. D. Cheronis, Virginia Bartow, L. L. Quill, M. V. McGill, N. W. Rakestraw, and P. H. Fall.

The following action was taken:

(1) Received and accepted treasurer's report.

(2) Mr. M. V. McGill, Chairman of the Committee on High-School Chemistry, gave a progress report on the work of his committee. Motion carried that the sum of $60 be allowed this Committee for necessary expenses between now and the month of September, 1941.

(3) Plans for the Divisional program for the A. C. S. meeting in Atlantic City next September were discussed.

PAUL H. FALL, *Secretary*

TREASURER'S REPORT—AUGUST 26, 1940–APRIL 2, 1941

Cash in bank, August 26, 1940	$287.70
Receipts from dues	153.00
Receipts from M. V. McGill from "Supplementary Experiments"	25.00
	$465.70
Expenditures:	
V. Bartow—to reimburse for outstanding bill paid by personal check	25.00
M. V. McGill—for work on "Outline of Chemistry"	61.97
Ira C. Davis, speaker at Detroit meeting	25.00
P. H. Fall—for office of secretary	25.00
J. CHEM. EDUC.—for reprints	42.73
Mack Printing Co.—letter heads	38.36
Ind. Eng. Chem.—abstracts Detroit meeting	22.20
L. J. Mitchell—dues for American Science Teachers' Association affiliation	5.00
M. V. McGill—for "Manual of Supplementary Experiments"	123.40
Ind. Eng. Chem.—abstracts for St. Louis meeting	22.20
	$390.86
Receipts less expenditures	74.84
Outstanding check	22.20
Sum of last two items equals bank balance April 2, 1941	97.04
Indebtedness:	
Committee on Examinations and Tests	50.00
V. Bartow—office of treasurer	10.05
Balance in Savings account, January 1, 1941	$310.12

VIRGINIA BARTOW, *Treasurer*

UNITED STATES CIVIL SERVICE EXAMINATIONS

THE Civil Service Commission has announced examinations for the following:

Principal Research Chemist (any specialized branch), $5600 a year

Senior Research Chemist (any specialized branch), $4600 a year

Research Chemist (any specialized branch), $3800 a year

Associate Research Chemist (any specialized branch), $3200 a year

Assistant Research Chemist (any specialized branch), $2600 a year

Applications will be rated as received at the Washington office of the United States Civil Service Commission until December 31, 1941, and certification made as the needs of the service require.

An insufficient number of eligibles is available for filling positions in certain specialized branches. Difficulty is being encountered in filling positions in the Bureau of Mines, Department of the Interior, and the Bureau of Agricultural Chemistry and Engineering, Department of Agriculture, in connection with the National Defense Program. Qualified persons with experience in chemical investigative work involving the use of recently developed specialized technics and instruments are urged to apply.

High-School Chemistry

An Integrated High School–College Chemistry Program

A. S. MICELI *Wayne University, Detroit, Michigan*

THE author makes no pretense at exhaustiveness nor any claim to originality of points included. This paper is the result of a continuous session with a year's supply of this JOURNAL, which procedure cannot but leave one with broad impressions of a nature that would not be expected from a month to month reading of the same material. No extensive references will be given. All one needs to do is consult the 1940 index for some twenty-five articles plus a number of pertinent editorials and letters on the general subject of course aims, context, and methods of teaching.

This sort of survey leaves one with the impression that among the currently espoused suggestions as to sound educational policies there are some of a distinctly perilous character, some of doubtful value, and some of fundamental and far-reaching worth. The first two types of policies appear to arise from an ill-defined and hazy national educational goal. However, out of all the views expressed comes a light which to the author appears to reveal a firm working hypothesis which should prove useful in deciding what phases of our science should be emphasized in high school and what phases should be emphasized in college.

By way of contrast to the main national educational goal, as discussed later, we may point out a few of the channels into which considerable energy appears to have been misdirected. We will then indicate a division of emphasis between the high school and the college which is consistent with the national goal.

FRUITLESS POLICIES

An undercurrent of thought existing in certain course-content studies would have us pin our hopes for a better day exclusively on a hierarchy of brains. However, an educational system designed only for the upper quarter of the student body is forgetting that the lower three quarters make possible the whole educational system in the first place. Faith in the prime value of a hyper-trained minority is simply another form of hero worship where that which is difficult to attain becomes by its very remoteness something highly desired and somehow also worth while. The few institutions which find themselves financially able to cater strictly to a select group are nevertheless producing students who must of necessity find their niche in a most commonplace world. My plea is not that we lower the high intellectual standards needed by the upper group for the comfort of the lower group. This could serve no good end. We must, however, recognize the material debt even if we dismiss totally the moral debt that we owe to the majority.

A second fruitless direction of our attention is toward such vague generalities as "softening the fiber of American youth" by removing "tedious drudgery" and the need for "desperate, determined striving." It is all too easy after ten to twenty years of association with a subject to expect beginners to learn and remember a large number of facts simply because the task requires a minimum of effort on the part of the specialist. How many new Chinese words could we learn day in and day out for eighteen weeks? For that matter, how many new English words do we add to our vocabulary every eighteen weeks even with effort—granting an intention. The effect on class mortality obtained by allowing this frame of mind to dominate our teaching might be construed as a wholesome operation of nature's laws—a survival of the fittest—especially if our will were strong enough to suppress our conscience. No, we cannot solve the broad educational problems of chemistry by drowning our students in work.

Another form of this intellectual inundation results from putting faith in the intrinsic worth of new and shining discoveries to get us going, though just where we are going, it is hard to say. I have no doubt but that many a high-school and freshman chemistry student has heard all about Pauling's theory of directed covalence. Fine, no doubt, for one or two geniuses who will see more than the teacher, but for the rest, merely a pretty cloud floating in thin air, coming from nowhere and going where all clouds go—wherever that may be.

POLICIES OF DOUBTFUL VALUE

First among the policies of questionable value is the tacit assumption that the man with the most degrees is alone qualified to think us out of our troubles. This contributes to the inferiority complexes of the high-school teachers and to some of the cockeyed ideas so common with people accustomed to looking out at the world along their noses. It is gratifying to see evidences of a rapidly growing number of people in all strata of scholastic attainment who are wasting no energy debating their right to ponder but who are using their energy directly on the job at hand.

An obvious corollary to the questionable attitude indicated above is to dismiss the conclusions obtained by one group of educators as being totally inapplicable to the needs of another. In this regard, all high-school and college teachers, regardless of what department

they may be in, should read the paper of Freud and Cheronis.[1]

A second avenue of escape from facing the irksome problem of deciding where we are going, is to be satisfied with preparing the student for the next course, which in turn will prepare the student for the next-next course which in turn—well, fortunately the student is soon graduated and through the graces of the gods his immense powers of adaptation carry him through. In this regard, we must agree that there is a chasm of difference between the attitude that general college chemistry, for example, should be designed specifically to anticipate the needs of subsequent courses and the attitude that having had general chemistry, one may profitably pursue more specialized work. The former attitude places emphasis on grinding out students technically prepared to study, let us say, qualitative analysis. The latter attitude emphasizes the value of arming the student with the perspective and orientation which a general chemistry course can give and thus preparing him psychologically and perhaps even (sh—just whisper this) philosophically for the more technical phases of his training.

A final questionable thesis is that to avoid a repetition of the high-school work in the freshman course means making a religious effort to exclude all but mere reference to topics specifically treated in the high school. In other words, we would be led to believe that drill and review on an important item are essential and laudable in one single course, but that the same important point must never be drilled and reviewed in any subsequent course. This frame of mind is convincingly debunked by a number of papers, in particular that by P. M. Glasoe.[2]

FUNDAMENTAL AIM. NATIONAL IDEAL

Leaving the blind alleys behind us, let us turn our attention directly to the inspired goal envisioned by the National Committee on Science Teaching as it is ably reported by R. L. Ebel.[3] "The principal job of the public schools is to prepare *all* of the children for effective living in a democracy." Science teaching must meet "directly and specifically . . . the personal and social needs of all the children . . . by developing such information, generalizations, skills, attitudes, and appreciations as are necessary for such things as critical thinking, intelligent consumption, conservation mindedness, health, safety consciousness, occupational perspective, recreational interest, a satisfying world picture and the support of scientific endeavor." This principal objective should motivate every course at all scholastic levels. We may now consider a suitable program for proceeding toward this goal.

[1] FREUD AND CHERONIS, "Retention in the physical science course," J. CHEM. EDUC., **17**, 289–93 (1940).

[2] GLASOE, "A high-school course in chemistry which does not lead to repetition in college," *ibid.*, **17**, 11–15 (1940). See also criticism and response, *ibid.*, **17**, 336–8 (1940).

[3] EBEL, "A report on the work of the National Committee on Science Teaching," *ibid.*, **17**, 249 (1940).

A DIVISION OF LABOR BETWEEN HIGH SCHOOL AND COLLEGE

In the first place let us admit to ourselves that the product of the American educational system is distinctly good. Our student is perhaps as free of prejudice as is anyone anywhere. He has breadth, and has as wholesome a world picture as can be expected in a mad world In view of the diversity of avenues followed by individual educators, this result can be attributed to one factor only. There must be few teachers, indeed, who are not sincerely interested in the welfare of our society. Some feel that they can best serve society by neglecting the majority in favor of the few, some feel that they must pile on the work, some feel that they must keep the student painfully up to date, and so on; but by far the most are sincere in their good intentions. Our point then is not to condemn the teacher for his choice of emphasis, but to suggest that it should be possible to make a shift of emphasis that will give richer returns for his efforts.

In a nutshell then, what shall be the significant difference in emphasis between the high school and college? It would seem that at the high-school level, the emphasis should be placed on inculcating the specific, widely accepted scientific facts and coördinating theories (to make the facts stick) which in the opinion of the instructor lead toward the democratic goal set up by the National Committee on Science Teaching. This emphasis on accepted knowledge shall overshadow any desire in the instructor to show clearly and logically what the nature of knowledge really is.

At the college level, on the other hand, the postulatory nature of the basic chemical theories should be emphasized. The college student should be keenly awake to the fact that knowledge is a man-made thing. He should have a firm appreciation of the fundamental difference between saying, for example, that the electron is a particle and saying that certain laboratory experiments lead us to believe that the electron has properties of the same character as a particle, but that we may not say *per se* that the electron *is* a particle. In other words, a college student should know the process by which we know what we think we do, while a high-school student should be required to go only the first step and learn the conclusions of the creators of our scientific knowledge.

Why this difference in emphasis? We may reasonably expect that additions to the body of basic scientific knowledge will be made by the college graduates. Before graduation, they should appreciate the exact nature of the thing to which they propose to add. Such students will be in an excellent position to combat the misconceptions promulgated by well-meaning Sunday supplement writers that science is an almighty machine that can answer any question if given enough time.

Am I advocating for the maturing college student a shift of emphasis from practicalities to daydreaming? Not at all! My thesis is that in placing insufficient

emphasis on the process by which our knowledge is obtained and the nature of the product of this process, we are neglecting a golden opportunity to help the student adjust himself to his inner misgivings, and to see that by the very nature of all that we know, there is no place for prejudice in our lives.

LETTERS

Frozen Stoppers

To the Editor:

May I suggest, with regard to M. Gordon Duvall's recent description of wrenching a frozen glass stopper from a bottle by force, that he use a bit of persuasion by first wetting the towel wound around the stopper and neck with hot water or steam.

As a matter of fact, I can recall hardly a stopper which has not come off meekly after simply heating the neck in a blast of steam or after dipping the stoppered end of the bottle momentarily in a beaker of boiling water. Also, one might immerse the entire bottle in hot water to cause an internal pressure helping to blow out the stopper. I have used this latter method (thanks to Professor A. A. Morton of M.I.T.) very successfully with frozen glass joints of reaction vessels by applying air pressure to the closed system while heating the frozen joint in a luminous flame.

May I alter a well-known proverb by suggesting that an ounce of persuasion is worth a pound of force.

GILBERT E. MOOS

51 ERKENBRECHER AVENUE
CINCINNATI, OHIO

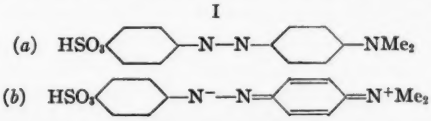
Action of Indicators

To the Editor:

In the article on "Phenolphthalein and Methyl Orange," by Peters and Redmon [J. CHEM. EDUC., **17**, 525 (1940)] it is reasonably stated that "the two colors of methyl orange would seem to call for two resonating mechanisms" but these authors were unable to arrive at a plausible resonance mechanism for the yellow form.

It is now suggested that the yellow (unacidified) dye resonates with I*a* and I*b* as principal extreme resonance configurations, this mechanism providing for the customary mobility of linkages within the conjugated chain.

I

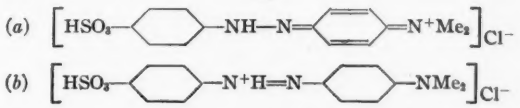


Although two configurations for I can be devised, this by no means implies that they are of the equal or nearly equal stability required for intense resonance. There are in fact three distinct factors which tend to render I*b* less stable than I*a* and which therefore cooperate to suppress resonance in I. These factors are (1) the instability of —N⁻— in I*b* (this nitrogen would not be expected to be very electronegative), (2) the coulombic interaction of the opposite charges in I*b* which tends to make the dipole unstable, and (3) the presence of the relatively unstable quinonoid arrangement in I*b* compared to the stable benzenoid arrangement in I*a*.

There is thus a strong tendency toward the classical configuration I*a* as has already been suggested by Lewis and Calvin [*Chem. Rev.*, **25**, 308 (1939)] who, however, give no detailed analysis of the problem. The result of this marked difference in stability between I*a* and I*b* is that resonance is considerably suppressed which corresponds to the relatively light color (yellow-orange) of the compound.

On acidifying the dye, the proton is most likely to become attached as shown in II as originally suggested by Hantzsch [*Ber.*, **41**, 1184 (1908); **42**, 2129 (1909)], and the resonance scheme II*a* ⟷ II*b* becomes possible.

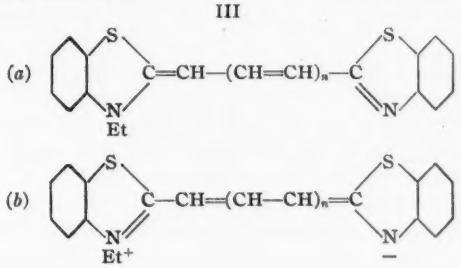
II



This is resonance of a modified amidinium ion type [> N—(C=C)$_n$—C=N$^+$ <] in which a cationic charge is shared between two nitrogen atoms, and is not subject to the resonance-suppressing influences (1) and (2) listed above in the case of I; and in spite of the fact that the third factor remains, II*a* and II*b* are sufficiently similar as regards stability for resonance in II to be strong enough to command a relatively deep color (red).

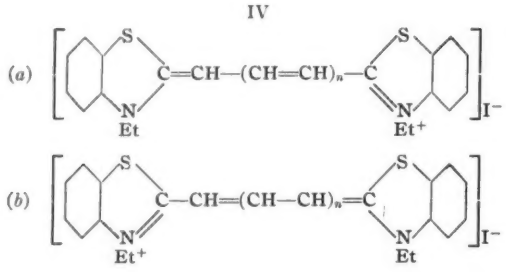
The essence of the indicator action of methyl orange is thus held to be replacement of a mode of resonance I*a* ⟷ I*b* which is weak because of a considerable difference in stability of the two extreme states, by the mode II*a* ⟷ II*b* which is much more strongly resonating because the two extreme states are much more nearly alike in stability.

III



The phenomenon therefore closely parallels that observed when anhydronium bases of the type of III are acidified or are treated with ethyl iodide to give the cyanines IV. The color of a base III is invariably

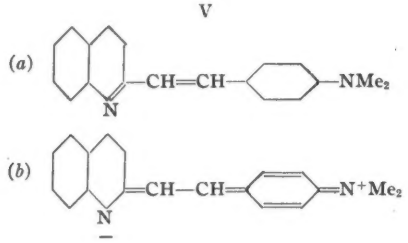
IV



deepened on adding ethyl iodide to give a cyanine IV and this is held to be due to substitution of the relatively weakly resonating system III*a* ⟷ III*b* by the intensely resonating system IV*a* ⟷ IV*b* (here the two extreme states are actually identical), but the amount of the shift in absorption depends on the value of *n* in the formulas [BROOKER, SPRAGUE, SMYTH, AND LEWIS, *J. Am. Chem. Soc.*, **62**, 1116 (1940)].

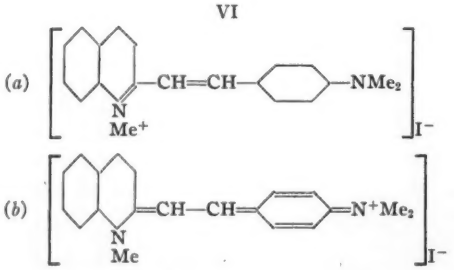
An even more closely related phenomenon is the halochromism of 2-*p*-dimethylaminostyrylquinoline (V).

V



This base, which is yellow, is deepened to wine-red on acidification or on conversion to the methiodide VI.

VI



Here again there is substitution of a weakly resonating system V*a* ⟷ V*b* for the more strongly resonating system VI*a* ⟷ VI*b* and the same three resonance-inhibiting factors given above for I also apply to V, while only one of these remains to restrict resonance in VI (factor 3), as was also the case with II.

To sum up, the deepening of color accompanying the acidification of a base such as I, III, or V is considered to be due to the fact that addition of a proton at the appropriate point enables the intensity of resonance within the conjugated system to be considerably increased.

A full discussion of the halochromism of V will shortly be published elsewhere.

LESLIE G. S. BROOKER
KODAK RESEARCH LABORATORIES
ROCHESTER, NEW YORK

Atomic Weight Unit

To the Editor:

Considerable interest has been shown recently in the matter of a name for the atomic weight unit. There seems to be no need for coining a new word to be added to the already long list of new words which the unhappy freshman chemistry student must assimilate.

Brinkley in "Introductory General Chemistry" calls this unit just what it is, "the Atomic Weight Unit." The unit is then defined as a weight which is one-sixteenth of the weight of the oxygen atom. This method of presentation seems to offer less difficulty to the beginning student than the method of presenting atomic weights as ratio numbers based upon the standard value of sixteen for oxygen.

The use of the term "Atomic Weight Unit" has a definite pedagogical advantage but I can see no reason for the use of such terms as "pel," "crith," etc.

WARD C. SUMPTER
WESTERN KENTUCKY STATE TEACHERS COLLEGE
BOWLING GREEN, KENTUCKY

Surface-Active Agents

To the Editor:

The classification of surface-active agents given by Professor Degering on page 102 of the March issue is quite interesting and useful. However, in the discussion of this tabulation and the classification of various commercial surface-active agents there appear to be inadvertencies.

Of the various types of agents, the most commonly used domestically is undoubtedly the A. 1 type (the common soaps), not the C. 1 type. The commercial products mentioned, Cue, Dreft, Drene, Irium, and Teel, are probably all of the B. 1 type, not of the C. 1 type. Dreft, Drene, and Irium are stated by the manufacturers to be alkyl sulfates. (See *Ind. Eng. Chem.*, **33**, 16 (1941), and H. L. Cupples, "A List of Commercially Available Detergents, Wetting, Dispersing, and Emulsifying Agents," Booklet E-504, Division of Insecticide Investigations, U. S. Department of Agriculture.)

The alkyl sulfates are easily distinguished from the alkyl sulfonates (C. 1 type) by their relative ease of hydrolysis on boiling in dilute hydrochloric acid.

CHARLES M. BLAIR, JR.
512 ATALANTA AVENUE
WEBSTER GROVES, MISSOURI

Out of the Editor's Basket

WE FEEL that one of the services that the JOURNAL offers to its readers is being overlooked. It concerns the availability of reprints. The JOURNAL is being continually more and more widely cited as a reference source. In keeping with its motto, "a living textbook of chemistry," it is intended that large numbers of students shall be directed to its pages. Every issue contains one article, at least, which merits citation to a class as collateral reading. A single bound volume is not adequate for such use; single copies in sufficient number may be too cumbrous, even. Many librarians find it convenient and satisfactory to put on the shelves a number of reprints of the articles cited.

In fact, reprints of appropriate articles are kept in stock for this very purpose. In the advertising pages of this issue will be found a list of the principal ones still available. You can doubtless find some that will be useful to you.

● Vernon C. Shippee, of Orange, California, sends us an account of a rather elaborate grading and classification system he uses for his class in high-school chemistry. It was devised in the effort to accord recognition to the faithful, plodding type of student, who does not do very well on examinations. The writer feels that a grading system should recognize all types of work and should give the student an incentive to go as far as possible in the things in which he is interested; should be open to inspection and discussion and enable the student to check his own progress. An analysis of the course showed that the following items should enter into the grading: experiments (both class and demonstration), laboratory projects, unknowns, problems (from the textbook and independent sources), oral report (on a subject selected by the teacher), a term paper, daily quizzes, occasional tests, final examination. To each of these items a certain number of "grade points" are assigned, from 5 for the oral report to 60 for the class experiments (credits on the latter item are given for writing up, as well as doing the experiment). A student may strive to increase his total grade point score by working on any of the various items, except that certain minima are required of all, to insure a reasonable distribution of effort. Finally, a certain number of total grade points are necessary for final grades of *A*, *B*, *C*, and *D*, respectively.

● From the Westinghouse laboratories comes the announcement of an improved "radium hound" to detect minute traces of radium, or other radioactive material. In principle it is an ionization chamber but differs from the older Geiger counter in that the faint current, resulting from the ions picked up, is amplified and read upon an indicating instrument calibrated directly in radioactive units. The "hound" is so sensitive that it will sniff out a mere few cents worth of radium.

● A little study made some time ago by E. F. Degering, of Purdue, should be of interest to all teachers who find themselves wondering occasionally whether the final examination is worth the trouble. He made a study of the distribution of grades in a class of 145 students, before and after the final examination. Only 22 students altered their positions by as much as one step in the grading scale, 13 going up and 9 down. The preliminary grades were based on an adequate number of tests and other data and the conclusion is that the final examination may be of value as a *teaching* tool but is of little value as a testing device. The objective examination used was an extensive one, made up of several parts, and an analysis showed that any one of the parts taken alone would have been as fair an examination as the whole. The important conclusion from this is that a few well-chosen items make as valid an examination as a large number.

● R. E. Dunbar, of North Dakota Agricultural College, recently made a survey of the problem content of twelve recent college textbooks of chemistry and discovered that there is a rather wide variation both in the number of problems in the various books and in the relative amount of space allotted to them. Problems involving reacting weights were the most numerous; the relative frequency of other types of problems was about the same, except for certain books which had a notable tendency to "specialize." Proportion, as a method of solution, was far more common than any other method. In comparison with high-school textbooks, college books make more use of problems, put more emphasis upon such topics as concentration of solutions, electrochemistry, solubility product, and equilibrium.

● There has recently been established a unique research institution at Pennsylvania State College. This is the Ellen H. Richards Institute, described as "a consolidated research unit to study certain aspects of the improvement of standards of living in the fields of food, clothing, and shelter." Three fields of research which have already been developed at the College will be continued in the new Institute: textile technology, human nutrition, and house construction.

The Institute is named after Ellen H. Richards, the first woman to receive a degree in chemistry at the Massachusetts Institute of Technology and the founder of household science in this country in its modern sense. The Director, Mrs. Pauline Beery Mack, will be assisted by an able group of colleagues.

● One of the newer developments of rubber is a tire tube which permits the passage of bullets, but because of its high inner surface tension immediately closes up the bullet holes with small loss of air. Airplane fuel tanks, on the same principle, have been standard equipment for some time.

● The extent of our efforts in the direction of defense education is indicated by a report by the Commissioner of Education indicating "that if present trends continue about 1,000,000 persons will have been trained for defense occupations by June 30, 1941." Enrolments in the regular vocational education program are highest in history, totaling approximately 2,000,000.

"In this far-reaching program millions of people in thousands of local communities of every State are working with heightened morale because they are actual participants in a great national effort," points out Commissioner Studebaker. "Twenty-three years of coöperation by the Federal, State, and local forces for vocational training have yielded real preparedness. In 1917–18 the newly sponsored vocational education system could train only 60,000 workers for war industries in 18 months. During the current year 23-year-old vocational education will train more than 1,000,000 in addition to the graduates of its regular courses."

● The U. S. Office of Education also announces a new national defense service to schools, entitled Information Exchange on Education and National Defense. Its purpose is to act as a central agency by which schools may share information about new or revised courses, training programs, or community educational activities valuable in connection with defense.

● Two little booklets have come to our attention, issued by Merck and Company. The first of these—"The Story of Amino Acids"—presents in very readable form a great deal of the latest information in this important chapter in biochemistry. The history and discovery of the amino acids is recounted, and their relation to the proteins, the methods for their isolation and synthesis, their identification and quantitative estimation, and their biochemical and physiological significance. The second booklet—"Vitamins in Nutrition"—is fresh off the press and, while it is by no means a complete monograph, will bring the reader up to date, painlessly. The recent syntheses of these substances are emphasized. Both these pamphlets, in their purpose as well as their content, are splendid contributions to chemical education in the larger sense and are typical of much that is coming out from some of the more progressive chemical manufacturing concerns.

● It has been pointed out that over $156,000,000 worth of dehydrated foods were required to meet conditions in this country in 1917, the first year of the last war. The manufacturers of dehydrated food products are organizing to anticipate even greater demands in the near future. That dehydrated foods are becoming more acceptable to the public is evidenced by the introduction of such recent items as dehydrated potatoes and dehydrated flavoring essences, such as onion and garlic. It is claimed that modern practices result in little if any loss in vitamins and important minerals.

● The new alloy, Kovar, developed in the Westinghouse laboratories, is finding a number of uses. Kovar is an alloy of iron, nickel, cobalt, and manganese, and has a coefficient of expansion practically the same as that of glass. It is now being put to use on a practical scale in the metal-to-glass seals in large vacuum tubes and X-ray tubes.

● "Duramin," recently developed in the Goodrich laboratories, has been announced as the latest thing in age-resisters for rubber. It is pointed out that one way of increasing our "production" of rubber is to make longer use of what we have. There is a lesson in that, during these hectic times.

● A new sound film entitled "It Isn't Done with Mirrors," featuring the development and production of synthetic resins, has been issued by the American Cyanamid and Chemical Corporation. It also shows some of the testing and development work in paper, leather, textiles, etc., in the Stamford laboratories. The film is available for use on application at the company's offices, 30 Rockefeller Plaza, New York City.

SUMMER CONFERENCE OF THE NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

FOLLOWING two very successful Summer Conferences, the New England Association of Chemistry Teachers is making plans for the Third Annual Conference to be held this summer on the campus of the University of Connecticut, Storrs, Connecticut, August 12–15, 1941. The morning and afternoon sessions will be devoted to invited papers on topics of current interest pertaining to the teaching of chemistry in secondary schools and colleges, and to recent advances in the science itself. Speakers of national repute have been invited to participate. Meals and lodging will be provided at a very low rate by the University, and accommodations for families will be available. A social program and industrial trips are being planned.

For further information concerning registration and reservations, address the Chairman of the Committee, Mr. G. B. Savage, Loomis School, Windsor, Connecticut.

RECENT BOOKS

ELECTRONIC PROCESSES IN IONIC CRYSTALS. *N. F. Mott*, M.A., F.R.S., and *R. W. Gurney*, M.A., Ph.D. First Edition. Oxford University Press, New York City, 1940. xii + 275 pp. 107 figs. 15 × 23 cm. $5.50.

Written by authors who have contributed much to the study of electronic and ionic processes in solids and solutions, this book maintains the standards of the International Series of Monographs on Physics of which it is a member. Beginning with a brief but clear presentation of current theory of interionic forces, lattice vibrations, and dielectric constants in perfect ionic crystals, the authors discuss in some detail the Frenkel and Wagner and Schottky theories of lattice defects. The remainder of the book consists of an extension of these theories to the explanation of the optical and electrical behavior of ionic crystals. The subjects discussed on this basis include electrolytic conductivity, absorption spectra and the absorption process, in particular in the alkali halides, photoconductivity and the photovoltaic effect, semiconductors and insulators, luminescence, and the photochemistry of silver halides with reference to latent image formation in the photographic process.

The explanations given are in large part qualitative although quantitative treatments are used whenever possible. A number of the developments are the authors' own—for example, the explanation of F-centers (p. 110), and of the photolytic process in silver halides (p. 229).

The book is designed primarily for advanced students, and an acquaintance with quantum mechanics and statistical mechanics, as well as thermodynamics and crystal structures, will be necessary for its complete understanding. On the other hand, the discussions are so clearly and interestingly written that a reader lacking these prerequisites could no doubt gain a great deal from the book, and it is recommended to anyone wishing to obtain a knowledge of the fundamental theory upon which present concepts of the processes of crystalline conduction, light absorption, luminescence, photographic latent image formation, etc., are based.

PHILIP A. LEIGHTON

STANFORD UNIVERSITY
STANFORD UNIVERSITY, CALIFORNIA

CHEMISTRY: A TEXTBOOK FOR COLLEGES. *W. McPherson, W. E. Henderson, W. C. Fernelius*, all of The Ohio State University, and *E. Mack, Jr.*, Battelle Memorial Institute. Ginn and Company, Boston, Massachusetts, 1940. viii + 762 pp. 379 figs. 15 × 23 cm. $3.75.

This latest edition of the McPherson-Henderson chemistry texts maintains the standard of excellence characteristic of the earlier ones of the series. It provides an introduction to the science adequate for the further study of chemistry, and is written in a style stimulating even to those who may not go beyond their first year in the subject.

Throughout the early chapters the authors skilfully apply a preliminary survey of the nature of atoms, molecules, and ions, "intended to serve the student as a guiding thread of simple but basic theory to tide him over until these important topics can be developed more fully in later chapters." This early emphasis on the particle nature of matter permits a novel approach to atomic weights through the positive ray method of measuring the relative weights of atoms—an innovation which brings out simply and effectively the significance of atomic weights. It is unfortunate that the derivation of formulas, the development of the concept of valence, and the introduction to oxidation-reduction have been merged with the chemistry of oxides in Chapter 11, Oxides and the Earth's Crust. The result is a chapter confusing to the student and misleading as to title.

An introduction to the Periodic Law by way of Moseley's experiments and atomic numbers is a refreshing change from the usual historical approach, and leads logically to an excellent presentation of the structure of the atom.

Modern concepts regarding the nature of salts, acids, and bases follow an introduction to ionization in solution through the Arrhenius' theory and its supporting evidence. Such an approach requires that classical theory be reconciled with the revelations of X-ray studies presented in an earlier chapter. This the authors do; but they do not bring out the inadequacy of the Arrhenius' theory for the interpretation of the colligative properties and conductance of solutions of strong electrolytes generally. Hence there is possible the misconception that the structure of electrovalent compounds is the sole reason for the development of the interionic attraction theory. The newer definitions of acid and base according to the Brønsted theory are included but not applied. Thus the hydrolysis of salts, appearing as an adjunct of a chapter on the Sulfur Family, is discussed in the traditional manner.

The descriptive chemistry of the non-metals follows the conventional plan based on their periodic placement. Metals, however, are assembled "in rather large groups based on their electromotive activities and the general plan of their metallurgy." Description of the latest industrial processes and the inclusion of an unusual amount of practical chemistry add to the interest in these chapters. Approximately eighty pages are given to organic chemistry.

Review questions and problems at the end of each chapter, together with references to standard books and journal articles, add to the usefulness of the text. Illustrations are abundant, and will be found valuable as aids to an understanding of the subjects discussed. Two of the innovations in this text may be a bit disturbing because of not being in accord with standard practice. The first of these is the omission of the period after the abbreviation of a scientific term; and the second is the use of "bound ions" to represent electrovalent compounds in equations for reactions, regardless of the medium in which the reaction occurs.

This text is modern in its treatment of the particle nature of matter, conservative in its application of solution theory, and unusual in the amount of descriptive chemistry it contains. The authors have shown that such chemistry can be interesting and intellectually stimulating. The book should find ready use among those who recognize the value of a substantial background in descriptive chemistry to both the future chemist and the general student.

HAROLD G. DIETRICH

YALE UNIVERSITY
NEW HAVEN, CONNECTICUT

SEMI-MICRO QUALITATIVE ANALYSIS. *C. J. Engelder*, Professor of Analytical Chemistry, University of Pittsburgh, *T. H. Dunkelberger*, Assistant Professor of Chemistry, Duquesne University, and *W. J. Schiller*, Head of Chemistry Department, Mount Mercy College. Second Edition. John Wiley and Sons, Inc., New York City, 1940. xii + 305 pp. 14.5 × 23 cm. $2.75.

This pioneer text in the field of semimicro qualitative analysis now appears in its second edition. [For review of the first edition, see J. CHEM. EDUC., **13,** 549 (1937).] During the past five years, the first edition has exerted a marked influence upon the teaching of qualitative analysis in the country. This is indicated by the relatively large number of new texts of qualitative analysis embodying the semimicro procedure and by the number of institutions employing this method. The second edition of this text continues to uphold the standards established in the first. It has been somewhat enlarged to include more material on modern concepts of solutions, more questions and problems, and additional laboratory procedures, especially in regard to anion analysis. In several places the laboratory procedures have been improved.

WARREN C. JOHNSON

UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

APPLICATIONS OF CHEMICAL ENGINEERING. Edited by *H. McCormack*, Professor of Chemical Engineering, Armour Institute of Technology. D. Van Nostrand Co., Inc., New York City, 1940. x + 431 pp. 15 × 23 cm. $3.75.

This text is a coöperative effort of the editor and twelve co-authors. Their aim has been to collect and unify the best available material on laboratory experiments for eleven of the unit operations of chemical engineering and to produce a practical laboratory manual. The authors have selected experiments that can be performed satisfactorily with simple equipment in a single laboratory period and which tie in definitely with the theoretical presentation of that unit operation.

The unit operations selected and the number of experiments for each are: measurement of temperature, 5 experiments; flow of fluids, 10; flow of heat, 6; evaporation and evaporators, 3; distillation, 6; drying of solids, 9; humidification and dehumidification, 3; gas absorption, 8; filtration, 6; classification and concentration of solids, 7; size reduction, 9.

This book is more than a mere laboratory manual, as each unit operation is introduced by sufficient theory and discussion to develop the formulas and show the significance of the variables to be measured in the experiments performed. Each experiment is divided into object, equipment needed, procedure (with alternatives), data to be taken, and the report. Although the chapters are not uniform in this respect, most of them give sample data and calculations necessary for the report.

Every chemical engineering instructor will desire a copy of this book, not only for the experiments he can use in his own course but also for the concise presentation of the operative theory given for each of the unit operations. Physical chemistry instructors will be interested in the chapters on measurement of temperature and distillation.

KENNETH A. KOBE

UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON

WHAT ARE THE VITAMINS? *W. H. Eddy*, Ph.D., Director, Good Housekeeping Bureau, Professor of Physiological Chemistry, Teachers College, Columbia University. Reinhold Publishing Corp., New York City, 1941. 247 pp. 15 figs. 15 × 23 cm. $2.50.

This book will be of great service to physicians, students of nutrition, and biochemists. It is, perhaps, a little too substantial and detailed for the general public. All of the vitamins known or reported are judicially discussed, even vitamins H, J, and P.

The historical treatment is generally thorough for a book of this size, although more could well have been written on vitamin A and carotene. Well-selected clinical reports and sound comments on them add considerably to the value of the book. Perhaps a stronger position on the optimum intake of vitamin C would have been advisable. The reviewer believes that a 24-hour urinary excretion of 40–50 mg. of this vitamin indicates a highly desirable factor of safety. As might be expected from Dr. Eddy, the tables of vitamin values are excellent.

This extremely valuable book is both readable and convincing. It deserves a large sale.

HARRY N. HOLMES

OBERLIN COLLEGE
OBERLIN, OHIO

HANDBOOK OF CHEMISTRY AND PHYSICS. *C. D. Hodgman*, M.S., Associate Professor of Physics at Case School of Applied Science, Editor; *H. N. Holmes*, Ph.D., Professor of Chemistry at Oberlin College, Associate Editor. Twenty-fourth Edition. The Chemical Rubber Co., Cleveland, Ohio, 1940. xviii + 2564 pp. 11.5 × 18 cm. $3.50.

This twenty-fourth edition of a standard handbook has all the usual chemical and physical data, and in addition has revisions and additions in the table of physical constants of organic compounds, the table of properties of commercial plastics, the list of physical constants of industrial organic compounds, a table of induced radioactivities, gravimetric factors and their logarithms (revised to correspond with recent changes in atomic weights), and minor changes to bring the data up to date.

SPECIFIC AND SPECIAL REACTIONS FOR USE IN QUALITATIVE ANALYSIS, WITH PARTICULAR REFERENCE TO SPOT TEST ANALYSIS. *F. Feigl*, Ph.D. Translated by *R. E. Oesper*, Ph.D., from a revision of the third German edition. First Edition. Nordemann Publishing Co., Inc., New York City, 1940. ix + 192 pp. 15 × 23 cm. $3.50.

Fritz Feigl is recognized as one of the pioneers in the development of the theory and use of complex compounds in analytical chemistry. Upon opening his "Qualitative Analysis by Spot Tests," this reviewer was keenly disappointed that the "Theoretical Part" had been omitted. The present text, so ably rendered into English by the translator, abundantly remedies this omission. In this text the author systematically and effectively presents a very large number of facts taken from his own work and that of others to lay a foundation for the theory pertinent to the analytical applications, particularly of complex compounds. After dealing with the analytically important types of complex compounds, the following topics are considered: Masking; Enhancement of Reactivity; Effect of Certain Atomic Groupings on Specific and Selective Activity; Effect of Certain Groups upon Solubility; Influence of Weighting Effects on Solubility; Capillary Phenomena; Fluorescence Analysis. The increased availability which this outstanding text now has should have the very desirable effect of stimulating interest and research in an ever more important field of chemistry.

W. W. RUSSELL

BROWN UNIVERSITY
PROVIDENCE, RHODE ISLAND

ANNUAL REVIEW OF BIOCHEMISTRY, Volume IX. *James Murray Luck*, Editor, and *James H. C. Smith*, Associate Editor. Annual Reviews, Inc., Stanford University Post Office, California, 1940. ix + 744 pp. 15 × 22.5 cm. $5.00.

Volume IX of the ANNUAL REVIEW OF BIOCHEMISTRY contains the following chapters: "Biological Oxidations and Reductions," K. G. Stern; "Proteolytic Enzymes," A. K. Balls; "Chemistry of the Carbohydrates and Glycosides," H. S. Isbell; "The Chemistry of the Acyclic Constituents of Natural Fats and Oils," J. A. B. Smith; "The Chemistry of the Lipins," E. Kirk; "The Chemistry of the Sterols," I. M. Heilbron and E. R. H. Jones; "Chemistry of Amino Acids and Proteins," D. I. Hitchcock; "The Chemistry and Metabolism of the Compounds of Sulfur," G. Toennies; "Fat Metabolism," H. J. Channon; "Carbohydrate Metabolism," W. H. Chambers and S. B. Barker; "The Metabolism of Proteins and Amino Acids," H. B. Lewis and R. L. Garner; "Clinical Applications of Biochemistry," V. C. Myers and E. Muntwyler; "Hormones," F. C. Koch; "Fat-Soluble Vitamins," H. Dam; "The Water-Soluble Vitamins," S. Lepkovsky; "The Biochemistry of Malignant Tissue," E. C. Dodds and F. Dickens; "Plant Pigments," G. Mackinney; "Aspects of Inorganic Metabolism in Plants," C. B. Lipman; "Soil Microbiology," S. A. Waksman; "Organic Acids of Plants," H. B. Vickery and G. W. Pucher; "The Biochemistry of Viruses," W. M. Stanley; "Biochemistry of the Lower Fungi," H. Raistrick; "The Application of Microchemistry to Biochemical Analysis," P. L. Kirk; "Insect Biochemistry," R. Craig and W. M. Hoskins; "Application of Radioactive Indicators in Biology," G. Hevesy; "Nonproteolytic Enzymes," H. Theorell.

The volume also contains author and subject indexes.

GARDENING WITHOUT SOIL. *A. H. Phillips*. Chemical Publishing Co., Inc., New York City, 1940. 137 pp. 8 figs. 13.5 × 22 cm. $2.00.

This book describes practical methods of growing plants of any kind and variety, in tanks of water, or in beds of sand and other minerals, to which are added plant foods in chemical form. It is written simply, yet gives complete technical data on every aspect of the problems involved.

LA GRANDE INDUSTRIE DES ACIDES ORGANIQUES. *Ulysse Roux* and *Albert Aubry*. Dunod, 92, Rue Bonaparte, Paris, France, 1939. viii + 378 pp. 16.5 × 25 cm.

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A new booklet, "The Water Treatment Science of Tomorrow in Today's Engineering," explains the theory of organic colloidal action and briefly discusses the modern trend in water treatment.

For this booklet write to *American K.A.T. Corporation, 122 East 42nd Street, New York, N. Y.*

The Focus

"The Educational Focus," a publication of the Bausch and Lomb Optical Company may be obtained by schools, colleges, and libraries, either through librarians or instructors (official stationery should be used in writing).

The following titles taken from Spring 1941 issue, represent the type of articles regularly appearing therein: The Playing Fields of Eton; Antireflection Films on Glass; Contributions of Microscopy to Photography; Thrips (Thysanoptera); Photographic Lantern Slides as a Student Project; Optical Briefs.

For further information, address *Bausch and Lomb Optical Company, Rochester, New York.*

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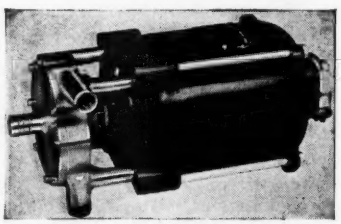

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New Bulletin on Convection Furnaces

A new 8 page bulletin #HD-341 entitled "Hevi Duty Multi-Range Convection Furnaces" is just published by the *Hevi Duty Electric Company, Milwaukee, Wisconsin.* The bulletin describes and illustrates the company's very complete line of convection furnaces. Copies of the bulletin are available free on request.